Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper(II)-photocatalyzed Decarboxylative Oxygenation of Carboxylic Acids

Alexander Reichle,[a] Hannes Sterzel, Peter Kreitmeier,[a] Remi Fayad,[b] Felix N. Castellano,*[b] Julia Rehbein*[a] and Oliver Reiser*[a]

[a.] Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany
E-Mail: oliver.reiser@chemie.uni-regensburg.de

[b.] Department of Chemistry, North Carolina State University, Raleigh,

North Carolina 27695-8204, United States.

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1 General Information

Commercially available chemicals were used without further purifications. Synthesized compounds were purified according to common standard procedures.[1] All photochemical reactions were carried out in oven-dried glassware. Reactions were carried out under atmospheric conditions unless stated otherwise. Petroleum ether (PE) and ethyl acetate (EtOAc) were distilled prior to use. The reported yields are refer to isolated compounds unless stated otherwise.

Chromatography

For thin-layer chromatography (TLC), precoated aluminum sheets (Merck silica gel 60 F_{254}) were used. UV light (λ = 254 nm) was applied for visualization. Staining was done with bromcresol green solution (0.040 g bromcresol green, 100 mL ethanol (95%), add NaOH solution (0.1 M), until pale blue color) and potassium permanganate (1.0 g $KMnO_4$, 2.0 g Na_2CO_3, 100.0 mL distilled water) followed by heating. Column chromatography was performed on silica gel (Merck, Geduran 80, 0.063 – 0.200 mm particle size) and flash silica gel (Merck, 0.040 – 0.200 mm particle size).

NMR-Spectroscopy

^{1}H-NMR- and ^{13}C-NMR Spectra were recorded on *Avance III* Systems of the Company Bruker, Rheinstetten:

- Bruker Avance 300 FT-NMR (for 300 MHz ^{1}H -NMR- and 75 MHz ^{13}C-NMR)
- Bruker Avance 400 FT-NMR (for 400 MHz ^{1}H -NMR- and 101 MHz ^{13}C-NMR and 377 MHz ^{19}F-NMR)

Field strengths are expressed in MHz and chemical shifts are reported relative to the solvent residual peak of commercially available NMR-solvents $CDCl_3$: δ ppm = 7.26; D_2O: δ ppm = 4.79 and DMSO-d_6: δ ppm = 2.5. The designation of the peak multiplicities is implemented as follow: s–singlet, d–doublet, dd–doublet of doublet, ddd–doublet of doublet of doublet, dt–doublet of triplet, dtd–doublet of triplet of doublet, t–triplet, td–triplet of doublet, q–quartet, p–pentet, m–multiplet.

IR-Spectroscopy

FTIR spectroscopy was performed on a Cary 630 FTIR spectrometer. Solid and liquid compounds were measured neat and the wave numbers are reported as cm^{-1}.

Mass Spectroscopy

Mass spectra were recorded by the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on a Varian MAT311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000 or Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS. High-resolution mass spectra were performed using electrospray ionization (ESI) or electron ionization (EI) with a quadrupole time-of-flight (Q-TOF) detector.

Melting Point

For melting point measurements an SRS MPA 100 OptiMelt was used with a heating rate of 1 °C/min.

X-ray

X-ray crystallographic analysis was performed by the Central Analytic Department of the University of Regensburg using an Agilent Technologies SuperNova, Agilent Technologies Gemini R Ultra, Agilent GV 50 or Rigaku GV 50. Suitable crystals were mounted on a Lindemann tube oil and kept at a steady temperature of T = 293 K during data collection. The structures were solved with the ShelXT (Scheldrick 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with ShelXL using Least Squares minimization.

Light Source

All photochemical reactions were performed using a LED-stick as irradiation source. The LED is placed on a glass rod (8 mm diameter; borosilicate glass; Schott Borofloat® 33) as fiber optics, which directly immerses in the reaction mixture. For the detailed reaction setup see Figure S1 in chapter 2.

UV light was performed using a Seoul Viosys CUN66A1B (3 W, 500 mA, λmax = 367 nm), NVSU233A (3 W, 700 mA, λmax = 367 nm) and a Luminus SST-10 (3 W, 720 mA, λmax = 365 nm or 405 nm).

Blue light irradiation was performed using an OSLO 80 rb (3 W, 700 mA, λmax = 455 nm), OSLO SSL 80 (3 W, 700 mA, λmax = 455 nm) or CREE XP rb LED (3 W, 700 mA, λmax = 455 nm). Green light irradiation was performed using an OSLON SSL 80 (3 W, 700 mA, λmax = 530 nm)

2 Photochemical Setup

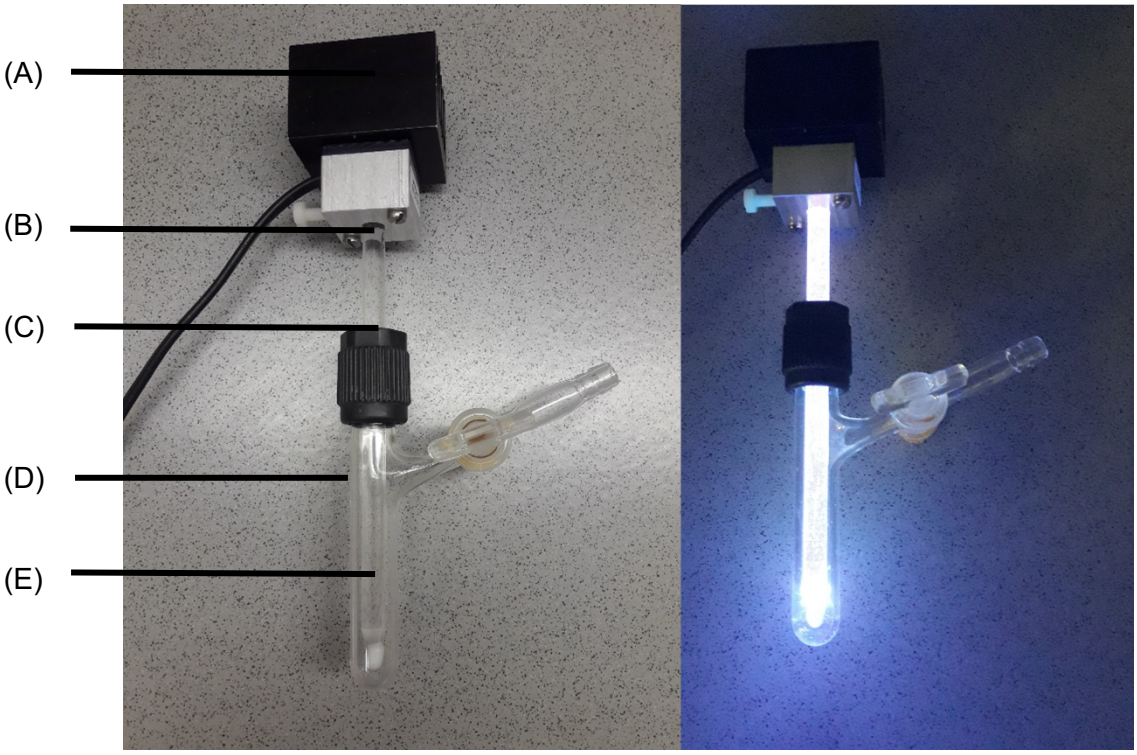


Figure S1: Irradiation setup for photochemical reactions: (A) LED; (B) glass rod; (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated stirring bar.

Determination of the radiant flux for the "Immersed light guide"

The radiant flux and emission spectra of the LED light sources, mounted on a glass or quartz rod (8 x = 150 mm), were determined using an integrating sphere (2π geometry) with an Avantes AvaSpec 3648 spectrometer, coupled with a fiber optic. The spectrometer response of this setup was referenced against LEDs with known radiant flux, determined independently with a calibrated FieldMate Power Meter, Edmund Optics.

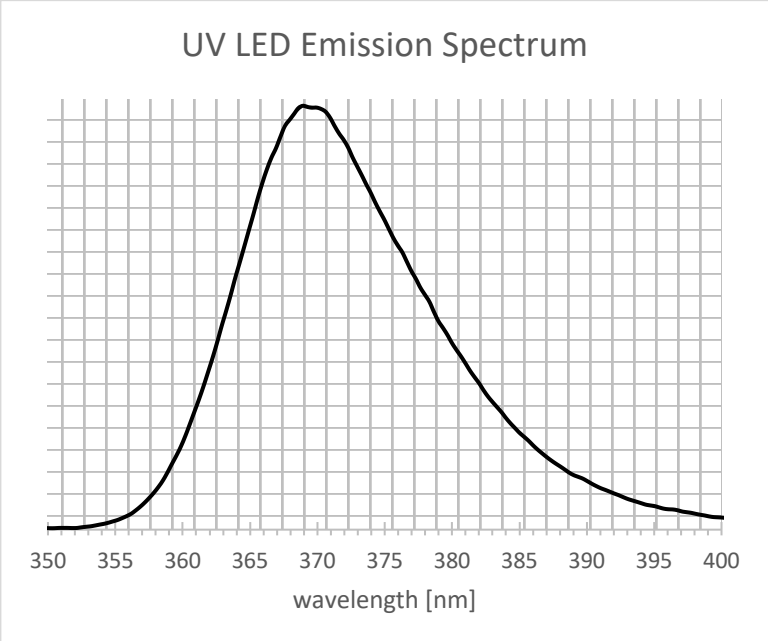
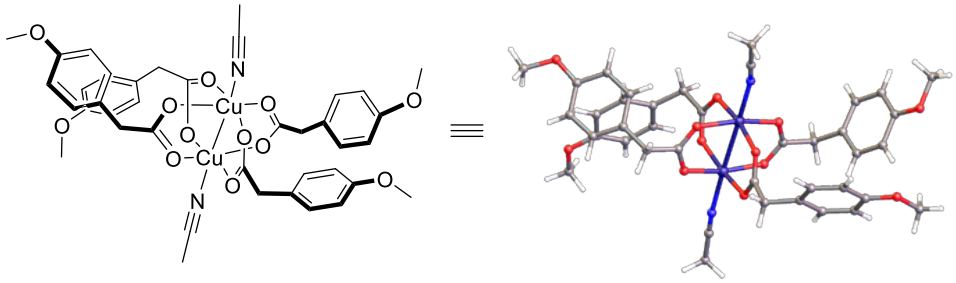


Figure S2: Emission Spectrum of Luminus SST-10.

3 Synthesis of Copper(II) Carboxylates

Cu_2(4-MeOpa)$_4$(MeCN)$_2$ (3)



The procedure for the synthesis of copper-carboxylate was slightly modified from the literature.[2] 4-methoxy phenylacetic acid (**1a**) (2.0 g, 12.0 mmol, 1.0 equiv) and 1M aq. NaOH (12.0 mL, 12.0 mmol, 1.0 equiv) were combined and sonicated for 5 minutes. Then copper(II)-sulfate pentahydrate (1.50 g, 6.02 mmol, 0.5 equiv) was added to the reaction mixture. The product precipitated immediately. After stirring for 30 min, the precipitate was collected by filtration and washed with water and diethyl ether. The precipitate was dried *in vacuo* for 3 h at 100 °C (heatgun), to afford copper(II) arylacetate (2.05 g, 86%) as parise-greenish powder.

Characterization of the copper(II) arylacetate precipitate:

mp: 215 °C (decomposition).

Elemental microanalysis (%): calculated for (Cu(**1a**)$_2$)$_n$ ≙ ($C_{18}H_{18}CuO_6$)$_n$: C 54.89, H 4.61 found: C 51.83, H 4.95.

IR (neat, cm^{-1}): 3541, 3429, 3008, 2914, 2840, 1580, 1513, 1464, 1431, 1401, 1304, 1248, 1177, 1032, 924, 861, 823, 738, 700.

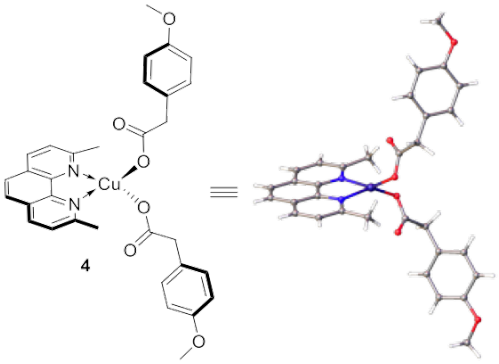
Single crystals suitable for X-ray analysis of the paddle-wheel complex (**3**) were obtained by crystallization of the precipitate *via* vapor diffusion of Et_2O into MeCN solution (1.0 mL).

mp: 205 °C (decomposition).

Elemental microanalysis (%): calculated for Cu_2(**1a**)$_4$(MeCN)$_2$ ≙ $C_{40}H_{42}Cu_2N_2O_{12}$: C 55.23, H 4.87 found: C 52.54, H 4.72.

IR (neat, cm^{-1}): 3046, 3000, 2937, 2911, 2836, 1584, 1513, 1464, 1394, 1300, 1244, 1177, 1107, 1032, 939, 857, 820, 730, 700.

Bis(2-(4-methoxyphenyl)acetoxy) neocuproino cuprate (4)



A round-bottomed flask was charged with copper(II) carboxylate (**3**) (200 mg, 508 µmol, 1.0 equiv) followed by addition of $CHCl_3$ (3 mL). The suspension was placed in an ultrasonic bath for 5 min. Afterward, neocuproine (106 mg, 508 µmol, 1.0 equiv) was added to the reaction mixture. A color change from dark greenish to bright greenish was observable. The reaction mixture was stirred for 1 h at 25 °C. Cold diethyl ether was added to precipitate the product. Filtration and subsequent drying *in vacuo* afforded the desired complex Cu(dmp)(4-MeOpa)$_2$ (**4**) as a bright greenish solid (291 mg, 483 µmol, 95%).

mp: 254 °C (decomposition).
IR (neat, cm^{-1}): 3026, 2989, 2840, 1595, 1509, 1446, 1358, 1300, 1274, 1241, 1177, 1148, 1107, 1025, 924, 861, 823, 685.
Elemental microanalysis (%): calculated for $C_{32}H_{30}CuN_2O_6$: C 63.83, H 5.02, N 4.65 found: C 62.97, H 5.04, N 4.55.
HRMS (ESI-MS) exact mass calc. for $[Cu(neocup)_2]^+$: m/z 479.1297, found: m/z 479.1311.

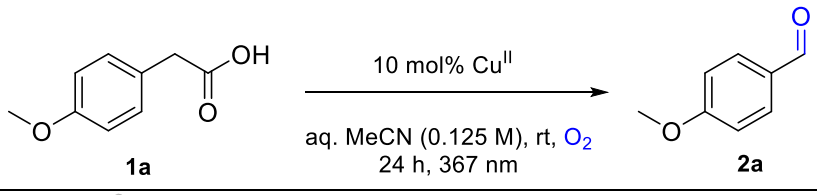
Single crystals suitable for X-ray analysis of copper complex (**4**) were obtained by vapor diffusion of pentane into $CHCl_3$ solution (1.0 mL). Selected bond lengths:

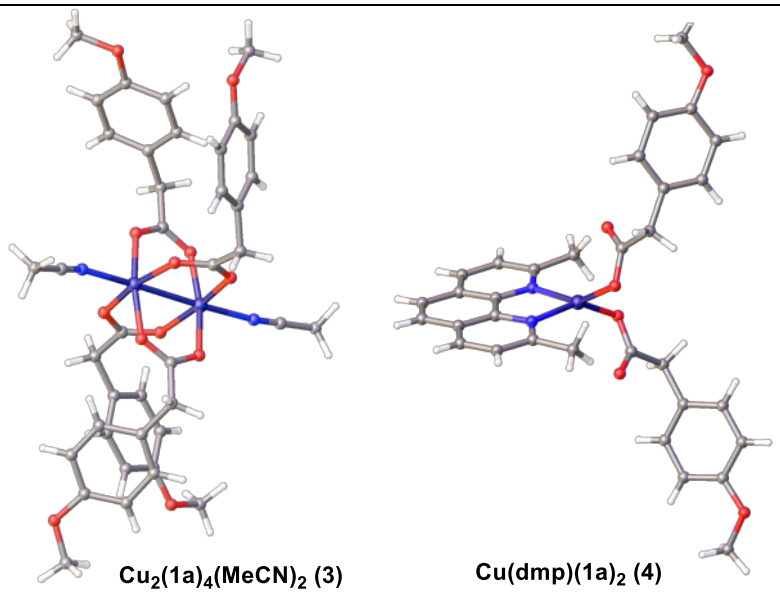
4 Reaction Optimization and Control Experiments

4.1 Initial Irradiation Experiments with Cu(II)-complexes

Reactions for optimization were performed on a 0.25 mmol scale in a 10mL Schlenk flask and ^{1}H-NMR yield is given. The reactions were performed with the setup shown in Figure S1, chapter 2. After the given time, the reaction mixture was concentrated *in vacuo* (200 mbar) and filtered over a pad of basic aluminum oxide. The filtrate was concentrated *in vacuo* (200 mbar) and the residue was dissolved in $CDCl_3$ and tetrachloroethane was added as internal standard. The yield was determined by integrating the characteristic peaks of the internal standard and the product.

Table S1: Initial Screening with Cu(II)-complexes.





$Cu_2(1a)_4(MeCN)_2$ (3) paddle-wheel coordination *vs.* **$Cu(dmp)(1a)_2$ (4)** monodendate coordination

Entry	Cu^{II} complex	Irradiation Power [mW]	Water Content [Vol%]	λ_{max} [nm]	Yield[b] (%)
1	$Cu_2(1a)_4(MeCN)_2$ (**3**)	160	-	367	11
2	$Cu_2(1a)_4(MeCN)_2$ (**3**)	160	2.2	367	21
3	$Cu(dmp)(1a)_2$ (**4**)	160	-	367	86
4	$Cu(dmp)(1a)_2$ (**4**)	160	2.2	367	91
5	no	160	-	367	10
6	$Cu(OAc)_2$ + dmp (*in situ*)	160	2.2	367	60

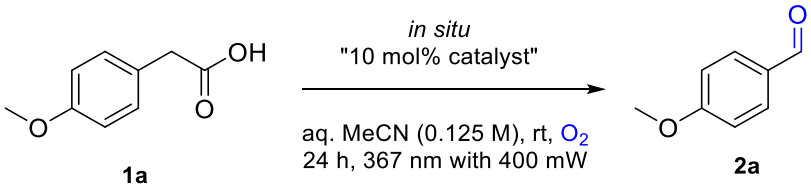
7	$Cu(OAc)_2$ + dmp (*in situ)*	400	2.2	367	95
8	$Cu(dmp)(1a)_2$ (**4**)	400	2.2	367	95
9[c]	$Cu(OAc)_2$ + dmp (*in situ)*	400	2.2	367	33
10[c]	no	400	2.2	367	nr

[a]Standard conditions: **1a** (0.25 mmol, 1.0 equiv), 10 mol% Cu^{II} (12.5 µmol, for complex **3** (Dimer) or 25 µmol, for complex **4**) in MeCN (2.0 mL, 0.125 M), water (45 µL, 2.2 Vol%), Irradiation at 367 nm with a radiant power of 160 mW under O_2 atmosphere for 24 h at room temperature (30 °C). [b]NMR yield using 1,1,2,2-tetrachloroethane as internal standard. [c]Reaction time was 2.5 h.

4.2 Irradiation Experiments for *in situ* Photocatalyst

Reactions for optimization were performed on a 0.25 mmol scale in a 10mL Schlenk flask and ^{1}H-NMR yield is given. The reactions were performed with the setup shown in Figure S1, chapter 2. After the given time, the reaction mixture was transferred to a round-bottomed flask and concentrated *in vacuo* (200 mbar). The residue was dissolved in $CDCl_3$ and tetrachloroethane was added as internal standard. The yield was determined by integrating the characteristic peaks of the internal standard and the product.

Table S2: Additional Parameter Screening.



Entry	Change from “standard conditions”	λ_{max} [nm]	Yield[b] (%)
1	With irradiation power of 160 mW	367	60
2	no changes	367	95 (93[c])
3	10 mol% of Cu(dmp)(**1a**)$_2$ as PC	367	95
4	With 10 mol% of Cu(OAc) instead of Cu(OAc)$_2$	367	94
5	Irradiation at 400 nm (irradiation power = 440 mW)	400	28
6	Irradiation at 455 nm (irradiation power = 550 mW)	455	23
7	dark	-	nr
8	Open to air	367	90
9	Under N_2 atmosphere	367	traces
10	Without water	367	83
11	water content of 0.2 Vol%	367	88
12	Water content of 10.3 Vol%	367	34
13	water content of 18.7 Vol%	367	44
14	MeCN (0.250 M)	367	88
15	MeCN (0.083 M)	367	95

[a]Standard conditions: 4-methoxyphenylacetic acid (**1a**) (0.25 mmol, 1.0 equiv), Cu(OAc)$_2$ (25 µmol, 10 mol%), dmp (2,9-dimethyl-1,10-phenanthroline) (25 µmol, 10 mol%) in MeCN (2.0 mL, 0.125 M), water (45 µL, 2.2 Vol%). Irradiation at 367 nm with a radiant power of 400 mW under O_2 atmosphere for 24 h at room temperature (30°C). [b]NMR yield using 1,1,2,2-tetrachloroethane as internal standard. [c]Isolated yield (0.5 mmol scale). nr = no reaction.

5 UV VIS Absorption Measurements

All UV-vis measurements were recorded on a SPECTRORECORD 200 PLUS of the company analytikjena using a Macro cell type 110-QS quartz cuvette with PTFE stopper (Hellma Analytics quartz cuvette, 10 × 10 mm, 3.5 mL).

For UV-Vis spectra of the Cu-complexes **3** and **4**, stock solutions with a concentration of $2.5 \cdot 10^{-3}$ mol/L. (referred to Cu(II)) were prepared. A volume of 200 µL was transferred to a cuvette, containing acetonitrile (2 mL) and water (45 µL). Then the spectra were recorded.

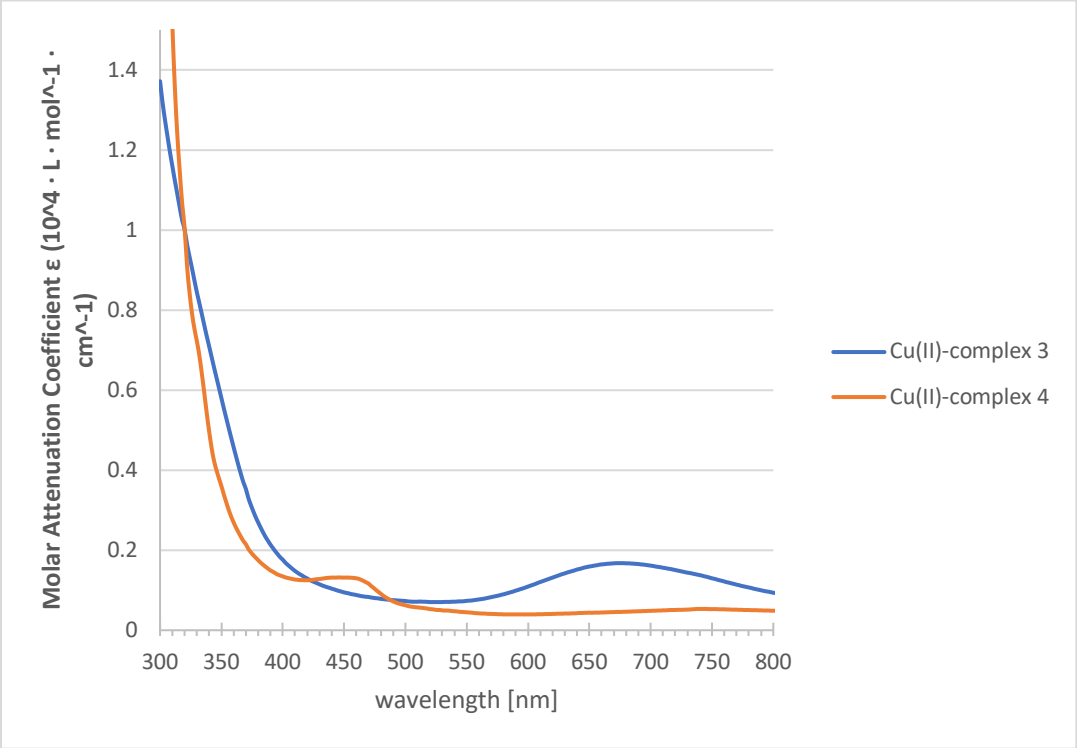


Figure S3: Absorption Spectra of Complexes Cu_2(**1a**)$_4$(MeCN)$_2$ (**3**) and Cu(dmp)(**1a**)$_2$ (**4**) in acetonitrile.

For UV-Vis monitoring (Figure S4), 4-methoxyphenylacetic acid (**1a**) (41.5 mg, 0.25 mmol, 1.0 equiv) and Cu(dmp)(**1a**)$_2$ (**4**) (15.1 mg, 25.0 µmol, 10 mol%) were dissolved in dry MeCN (2.0 mL, 0.125 M) and water (45 µL, 2.2 Vol%). The mixture was irradiated at 367 nm under O_2 atmosphere for 24 h at room temperature (30 °C). After 24h, 10 µL of the reaction mixture was dissolved into 2 mL of acetonitrile, showing the typical absorption at 450 nm for $[Cu(I)(dmp)]^+$ (*cf.* Scheme 2, main part). UV-Vis spectra of **1a** and the product **2a** showed no increased absorbance at 367 and 450 nm.

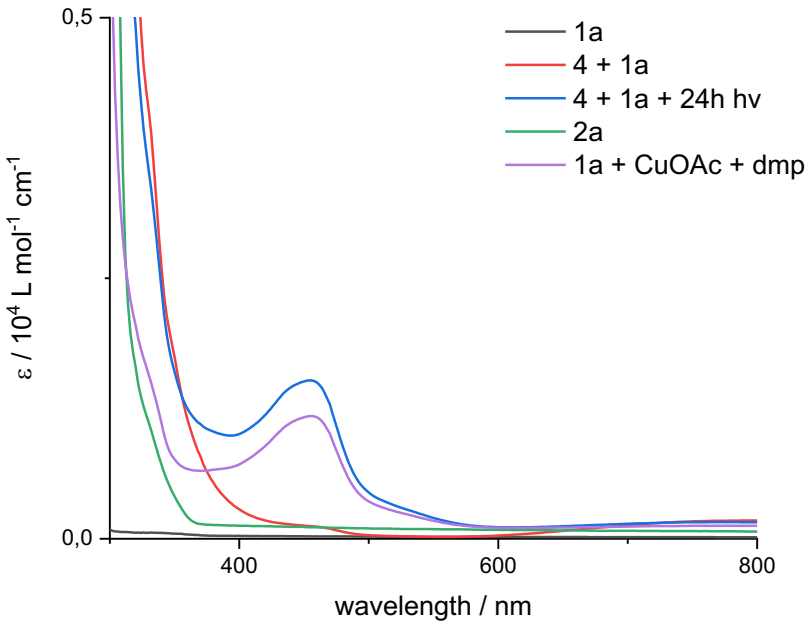
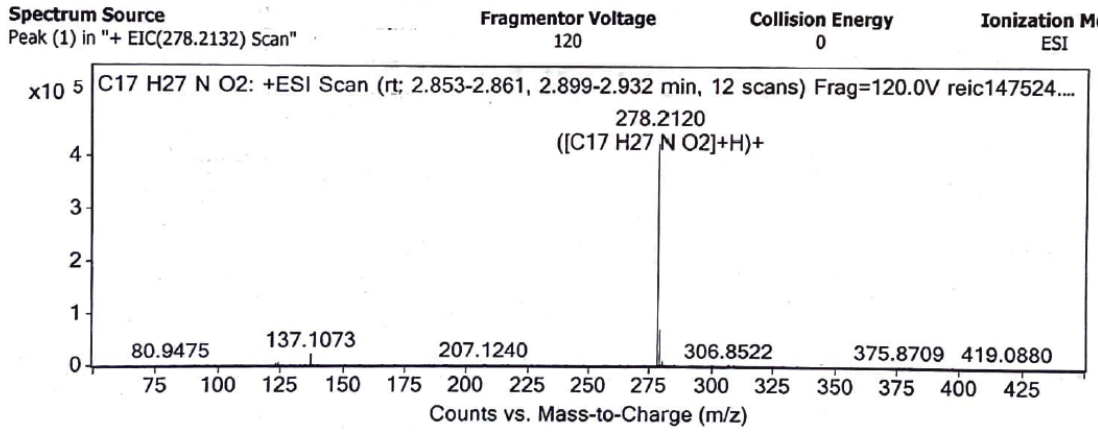


Figure S4: UV-Vis monitoring of the reaction solution and absorbance spectra of **1a** and **2a**.

6 Radical Trap Experiment and Reaction under N_2-Atmosphere

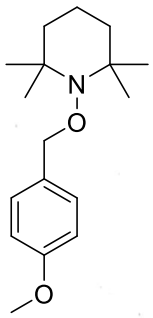
6.1 TEMPO Trapping

For TEMPO trapping experiments, 4-methoxyphenylacetic acid (**1a**) (41.5 mg, 0.25 mmol, 1.0 equiv) and Cu(dmp)(**1a**)$_2$ (**4**) (15.1 mg, 25.0 µmol, 10 mol%) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (46.9 mg, 0.30 mmol, 1.2 equiv) were dissolved in dry MeCN (2.0 mL, 0.125 M) and water (45 µL, 2.2 Vol%). The mixture was irradiated at 367 nm under O_2 atmosphere for 24 h at room temperature (30°C).



Peak List

m/z	z	Abund	Formula	Ion
123.0915		4011.93		
124.088	1	5014.13		
126.1278	1	1064.01		
137.0598	1	5358.82		
137.1073	1	21078.88		
138.1103	1	1756.84		
151.1216	1	925.1		
207.124	1	1082.74		
262.8885		1048.68		
278.212	1	423226.25	C17 H27 N O2	(M+H)+
279.2157	1	69601.73	C17 H27 N O2	(M+H)+



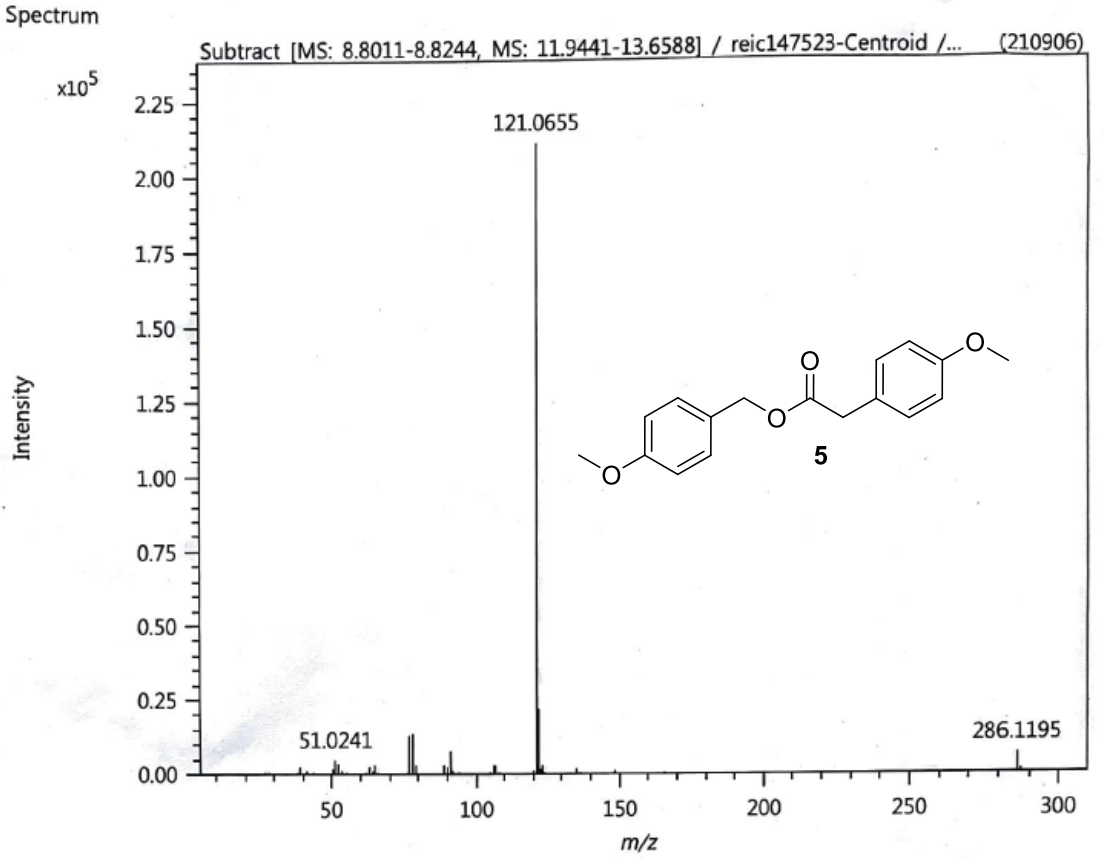
TEMPO-adduct

Figure S5: HRMS of TEMPO trap experiment (crude reaction mixture was submitted for analysis).

The decarboxylation reaction is completely suppressed and the TEMPO-adduct was observed by ESI-HRMS (calc. for $C_{17}H_{27}NO_2$ $[M+H]^+$: 278.2115, found 278.2120). The result indicates the formation of free radicals in the mechanistic pathway.

6.2 Reaction under N_2-Atmosphere

For the reaction under N_2-atmosphere, 4-methoxyphenylacetic acid (**1a**) (0.25 mmol, 1.0 equiv), $Cu(OAc)_2$ (25 µmol, 10 mol%) and dmp (2,9-dimethyl-1,10-phenanthroline) (25 µmol, 10 mol%) were dissolved in dry MeCN (2.0 mL, 0.125 M), water (45 µL, 2.2 Vol%). The reaction mixture was degassed three times applying freeze-pump-thaw-cyles. Irradiation at 367nm under N_2 atmosphere for 24 h at room temperature (30°C).



Elemental Composition

Parameters		Elements:							
Tolerance:	10.00 ppm	Symbol	C	H	N	O	Cl	S	Se	Sen
Electron:	Odd/Even	Min	0	0	0	0	0	0	0	0
Charge:	+1	Max	100	100	0	5	0	0	0	0
DBE:	-1.5 - 50.0									

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
286.11953	6713.13	C17 H18 O4	286.11996	-0.43	-1.52	9.0

Figure S6: HRMS of Reaction under N_2-Atmosphere (crude reaction mixture was submitted for analysis).

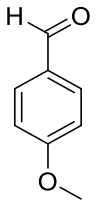
7 General Procedure for Cu(II)-photocatalyzed Decarboxylative Oxygenation of Carboxylic Acids (GP-A)

A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with anhydrous $Cu(OAc)_2$ (4.5 mg, 25 µmol, 10 mol%), dmp (5.2 mg, 25 µmol, 10 mol%) and the carboxylic acid (0.25 mmol, 1.0 equiv)**.** Subsequently, the solvent mixture MeCN (2.0 mL) and water (45 µL, 2.2 Vol%) was added. The reaction tube was flushed with oxygen and a balloon containing oxygen was added. A Teflon sealed inlet for a glass rod was placed on the reaction tube, through which irradiation with LED took place from above. The mixture was stirred in an aluminum block at room temperature (30 °C) for 24 h; for a detailed setup see Figure S1, chapter 2. The reaction was monitored by TLC. Afterwards, two equal reaction mixtures were united and the solvent was removed under reduced pressure (200 mbar) to afford the crude.

Two different work-up procedures were used. Work-up Procedure A: The residue was dissolved in DCM/ EtOAc and the solution was filtered through a pad of basic aluminum oxide (washed three times) and the filtrate was concentrated *in vacuo* (200 mbar).

Work-up-Procedure B: The residue was purified by flash column chromatography on silica gel (eluent PE/ EtOAc).

4-methoxybenzaldehyde (2a)



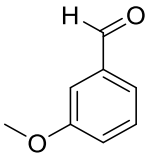
Following general procedure (GP-A) using 4-methoxyphenylacetic acid (**1a**) (83.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) in the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm; radiant power of 400 mW) for 24 h yielded 63.5 mg (446 µmol, 93%) of 4-methoxylbenzaldehyde (**2a**) as a colorless oil, using work-up procedure A. Spectral data are in accordance to literature.[3]

R*f* (5:1 PE/EtOAc) = 0.51.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 9.85 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 190.9, 164.7, 132.0, 130.0, 114.4, 55.6.

3-methoxybenzaldehyde (2b)



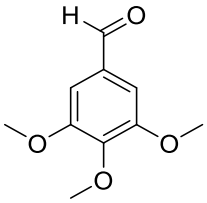
Following general procedure (GP-A) using 3-methoxyphenylacetic acid (**1b**) (83.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 60.0 mg (441 µmol, 88%) of 3-methoxybenzaldehyde (**2b**) as a colorless oil, using work-up procedure A. Spectral data are in accordance to literature.[4]

R_f (5:1 PE/EtOAc) = 0.57.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 9.98 (s, 1H), 7.49 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 7.22 – 7.14 (m, 1H), 3.87 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 192.3, 160.3, 137.9, 130.2, 123.7, 121.7, 112.1, 55.6.

3,4,5-trimethoxybenzaldehyde (2c)



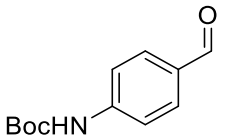
Following general procedure (GP-A) using 3,4,5-trimethoxyphenylacetic acid (**1c**) (113.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 83.8 mg (427 µmol, 85%) of 3,4,5-trimethoxybenzaldehyde (**2c**) as a white solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[5]

R_f (5:1 PE/EtOAc) = 0.24.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 9.83 (s, 1H), 7.09 (s, 2H), 3.89 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 191.1, 153.7, 143.6, 131.8, 106.8, 61.0, 56.3.

tert-butyl (4-formylphenyl)carbamate (2d)



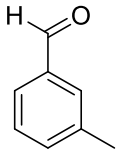
Following general procedure (GP-A) using 2-(4-((tert-butoxycarbonyl)amino)phenyl)acetic acid (**1d**) (125.6 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 107.3 mg (485 µmol, 97%) of tert-butyl (4-formylphenyl)carbamate (**2d**) as a white solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[6]

R*f* (5:1 PE/EtOAc) = 0.39.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 9.88 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 6.94 (s, 1H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 191.1, 152.2, 144.4, 131.4, 131.4, 117.9, 81.6, 28.4.

3-methylbenzaldehyde (2e)



Following general procedure (GP-A) using 3-methylphenylacetic acid (**1e**) (83.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 53.3 mg (444 µmol, 89%) of 3-methylbenzaldehyde (**2e**) as a pale yellow oil, using work-up procedure B (PE / EtOAc 1:2).

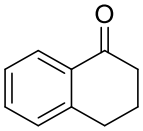
Spectral data are in accordance to literature.[3]

R*f* (5:1 PE/EtOAc) = 0.82.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 9.96 (s, 1H), 7.49 – 7.36 (m, 3H), 7.17 (dt, *J* = 5.9, 2.8 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 192.3, 160.3, 138.0, 130.2, 123.7, 121.7, 112.2, 55.6.

3,4-dihydronaphthalen-1(2H)-one (2h)



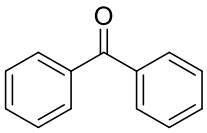
Following general procedure (GP-A) using 1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (**1h**) (88.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 60.3 mg (412µmol, 82%) of 3,4-dihydronaphthalen-1(2H)-one (**2h**) as a yellowish oil, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[8]

R*f* (5:1 PE/EtOAc) = 0.67.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.66 (dd, *J* = 7.3, 5.8 Hz, 2H), 2.14 (p, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 198.5, 144.6, 133.5, 132.8, 128.9, 127.3, 126.8, 39.3, 29.9, 23.4.

benzophenone (2i)



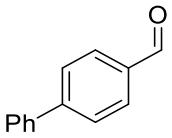
Following general procedure (GP-A) using 2,2-diphenylacetic acid (**1i**) (106.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 90.2 mg (495 µmol, 99%) of benzophenone (**2i**) as a colorless oil, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[8]

R*f* (5:1 PE/EtOAc) = 0.60.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.84 – 7.77 (m, 4H), 7.62 – 7.56 (m, 2H), 7.55 – 7.44 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 196.8, 137.6, 132.4, 130.1, 128.3.

[1,1'-biphenyl]-4-carbaldehyde (2j)



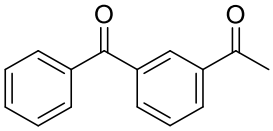
Following general procedure (GP-A) using 2-([1,1'-biphenyl]-4-yl)acetic acid (**1j**) (106.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 160 mW) for 24 h yielded 68.8 mg (378 µmol, 76%) of [1,1'-biphenyl]-4-carbaldehyde (**2j**) as a white solid, using work-up procedure B (PE / EtOAc 10:1). Spectral data are in accordance to literature.[5]

R*f* (10:1 PE/EtOAc) = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 10.06 (s, 1H), 8.00 – 7.91 (m, 2H), 7.79 – 7.72 (m, 2H), 7.68 – 7.60 (m, 2H), 7.53 – 7.44 (m, 2H), 7.47 – 7.37 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 192.1, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

1-(3-benzoylphenyl)ethan-1-one (2k)



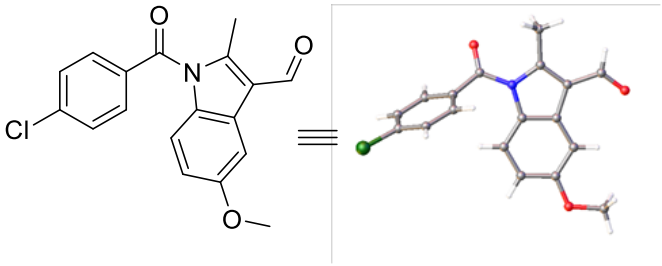
Following general procedure (GP-A) using 2-(4-benzoylphenyl)propanoic acid (ketoprofen) (**1k**) (134.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 74.5 mg (332 µmol, 66%) of 1-(3-benzoylphenyl)ethan-1-one (**2k**) as a white solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[5]

R*f* (5:1 PE/EtOAc) = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.36 (td, *J* = 1.8, 0.6 Hz, 1H), 8.18 (ddd, *J* = 7.8, 1.8, 1.2 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.82 – 7.76 (m, 2H), 7.65 – 7.57 (m, 2H), 7.54 – 7.45 (m, 2H), 2.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 197.4, 196.0, 138.2, 137.3, 137.1, 134.4, 133.0, 131.9, 130.2, 129.8, 128.9, 128.6, 26.9.

1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-carbaldehyde (2l)



Following general procedure (GP-A) using indometacine (**1l**) (178.9 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 160 mW) for 24 h yielded 76.5 mg (223 µmol, 47%) of 1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-carbaldehyde (**2l**) as a white crystalline solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[5]

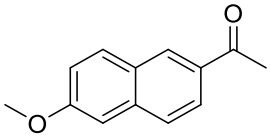
R*f* (5:1 PE/EtOAc) = 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 10.32 (s, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.53 – 7.47 (m, 2H), 6.73 (d, *J* = 1.6 Hz, 2H), 3.87 (s, 3H), 2.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 185.9, 168.4, 157.3, 148.6, 141.1, 132.2, 131.8, 130.8, 129.6, 127.1, 118.5, 114.4, 114.0, 103.5, 55.9, 12.8.

Single crystals suitable for X-ray analysis compound **2l** were obtained by crystallization from $CHCl_3$ (1.0 mL).

1-(6-methoxynaphthalen-2-yl)ethan-1-one (2m)



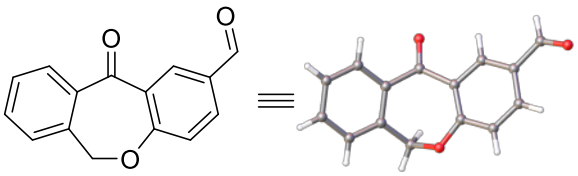
Following general procedure (GP-A) using 2-(6-methoxynaphthalen-2-yl)propanoic acid/ naproxene (**1m**) (115.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(Oac)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 99.7 mg (498 µmol, 99%) of 1-(6-methoxynaphthalen-2-yl)ethan-1-one (**2m**) as a white crystalline solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[9]

R*f* (5:1 PE/EtOAc) = 0.36.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 8.38 (d, *J* = 1.8 Hz, 1H), 8.00 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.84 (dt, *J* = 8.9, 0.7 Hz, 1H), 7.79 – 7.70 (m, 1H), 7.20 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 2.69 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 198.0, 159.8, 137.4, 132.7, 131.2, 130.2, 127.9, 127.2, 124.8, 119.8, 105.8, 55.5, 26.7.

11-oxo-6,11-dihydrodibenzo[b,e]oxepine-2-carbaldehyde (2n)



Following general procedure (GP-A) using 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetic acid (**1n**) (134.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(Oac)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 160 mW) for 24 h yielded 67.0 mg (281 µmol, 56%) of 11-oxo-6,11-dihydrodibenzo[b,e]oxepine-2-carbaldehyde (**2n**) as a yellowish solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[5]

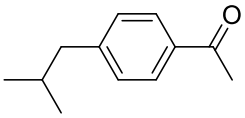
R*f* (5:1 PE/EtOAc) = 0.33.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 9.97 (s, 1H), 8.71 (d, *J* = 2.2 Hz, 1H), 8.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.59 (td, *J* = 7.4, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 190.3, 165.6, 140.4, 137.5, 134.6, 133.5, 133.3, 131.0, 129.8, 129.5, 128.3, 125.1, 122.3, 73.7.

Single crystals suitable for X-ray analysis compound **2n** were obtained by crystallization from $CHCl_3$ (1.0 mL).

1-(4-isobutylphenyl)ethan-1-one (2o)



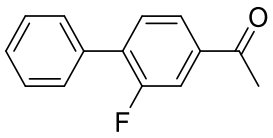
Following general procedure (GP-A) using 2-(4-isobutylphenyl)propanoic acid / ibuprofen (**1o**) (115.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 86.0 mg (488 µmol, 98%) of 1-(4-isobutylphenyl)ethan-1-one (**2o**) as a colorless oil, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[3]

R*f* (5:1 PE/EtOAc) = 0.83.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] =7.91 – 7.80 (m, 2H), 7.25 – 7.20 (m, 2H), 2.58 (s, 3H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.89 (dt, *J* = 13.9, 7.0 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 198.0, 147.7, 135.1, 129.4, 128.4, 45.5, 30.2, 26.7, 22.4.

1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (2p)



Following general procedure (GP-A) using 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid / fluorbiprofen (**1p**) (122.1 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 100.7 mg (470 µmol, 94%) of 1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (**2p**) as a white crystalline solid, using work-up procedure B (PE / EtOAc 10:1). Spectral data are in accordance to literature.[5]

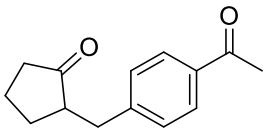
R*f* (10:1 PE/EtOAc) = 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.74 (dd, *J* = 11.1, 1.7 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 196.5 (d, *J* = 1.9 Hz), 159.8 (d, *J* = 249.9 Hz), 137.9 (d, *J* = 6.5 Hz), 134.8 (d, *J* = 1.6 Hz), 133.9 (d, *J* = 13.7 Hz), 131.0 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 3.1 Hz), 128.7, 128.6, 124.4 (d, *J* = 3.5 Hz), 116.0 (d, *J* = 24.0 Hz), 26.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ [ppm] = -117.19 (ddt, *J* = 9.2, 7.5, 1.9 Hz).

2-(4-acetylbenzyl)cyclopentan-1-one (2q)



Following general procedure (GP-A) using 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (**1q**) (123.2 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 106.5 mg (492 µmol, 98%) of 2-(4-acetylbenzyl)cyclopentan-1-one (**2q**) as a colorless oil, using work-up procedure B (PE / EtOAc 3:1).

R*f* (3:1 PE/EtOAc) = 0.35.

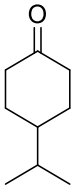
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.85 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.15 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.55 (s, 3H), 2.38 – 2.21 (m, 2H), 2.14 – 2.01 (m, 2H), 1.99 – 1.87 (m, 1H), 1.78 – 1.64 (m, 1H), 1.50 (dtd, *J* = 12.5, 11.0, 6.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 219.5, 197.8, 145.9, 135.4, 129.2, 128.6, 50.7, 38.1, 35.6, 29.2, 26.6, 20.6.

IR (neat, cm^{-1}): 2963, 2877, 2363, 1736, 1681, 1606, 1572, 1412, 1360, 1267, 1185, 1121, 1017, 957, 861, 820, 693.

HRMS (EI-MS) exact mass calc. for $C_{14}H_{16}O_2$ $[M]^{\cdot+}$ m/z 216.11448, found: m/z 216.11411.

4-isopropylcyclohexan-1-one (2r)



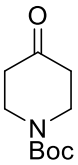
Following general procedure (GP-A) using 4-isopropylcyclohexane-1-carboxylic acid (**1r**) (85.2 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 39.9 mg (285 µmol, 57%) of 4-isopropylcyclohexan-1-one (**2r**) as a colorless smelly oil, using work-up procuedure B (PE / EtOAc 10:1). Spectral data are in accordance to literature.[10]

R*f* (5:1 PE/EtOAc) = 0.54. Vanillin-Stain.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 2.48 – 2.21 (m, 4H), 2.05 – 1.91 (m, 2H), 1.61 – 1.38 (m, 4H), 0.92 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 212.8, 42.7, 41.2, 31.9, 29.8, 20.1.

tert-butyl 4-oxopiperidine-1-carboxylate (2s)



Following general procedure (GP-A) using 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid (**1s**) (114.6 mg, 0.5 mmol, 1.0 equiv), dmp (10.4 mg, 50 µmol, 10 mol%), dry $Cu(OAc)_2$ (9.1 mg, 50 µmol, 10 mol%) and the solvent mixture at room temperature (30 °C) and irradiation with UV-LED (λ_{max}= 367 nm, radiant power of 400 mW) for 24 h yielded 72.0 mg (361 µmol, 72%) of tert-butyl 4-oxopiperidine-1-carboxylate (**2s**) as a colorless solid, using work-up procedure B (PE / EtOAc 5:1). Spectral data are in accordance to literature.[11]

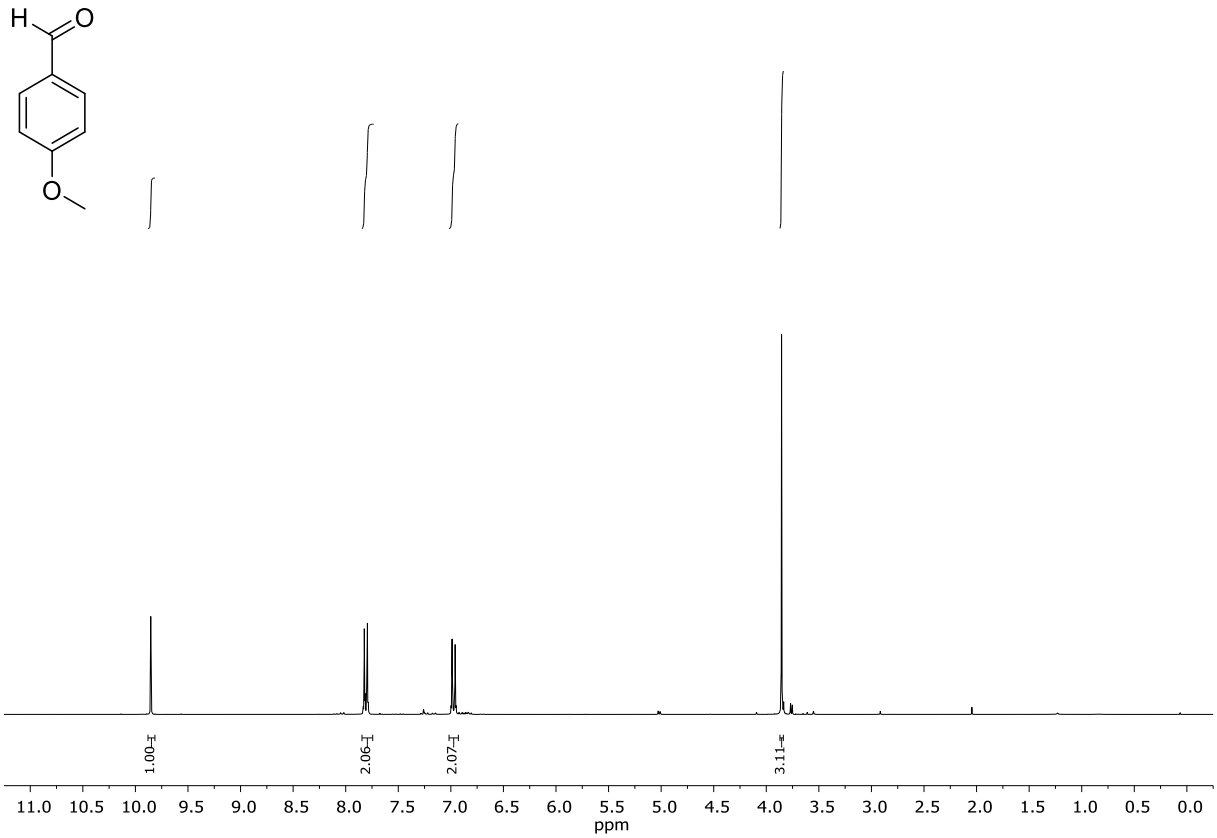
R*f* (5:1 PE/EtOAc) = 0.34. Vanillin-Stain.

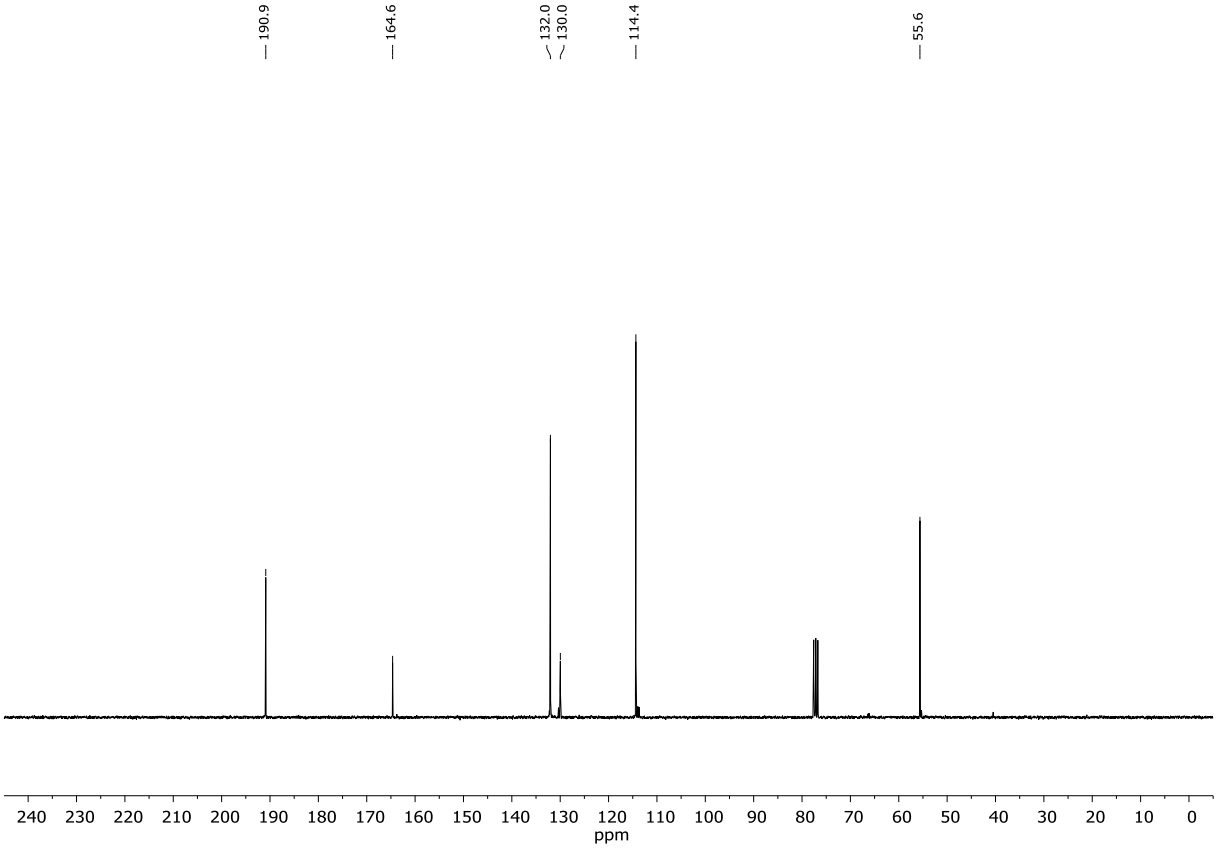
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 3.70 (t, *J* = 6.2 Hz, 4H), 2.42 (t, *J* = 6.2 Hz, 4H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 208.0, 154.7, 80.6, 43.1, 41.3, 28.5.

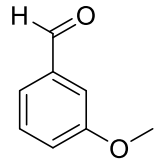
8 Copies of NMR spectra

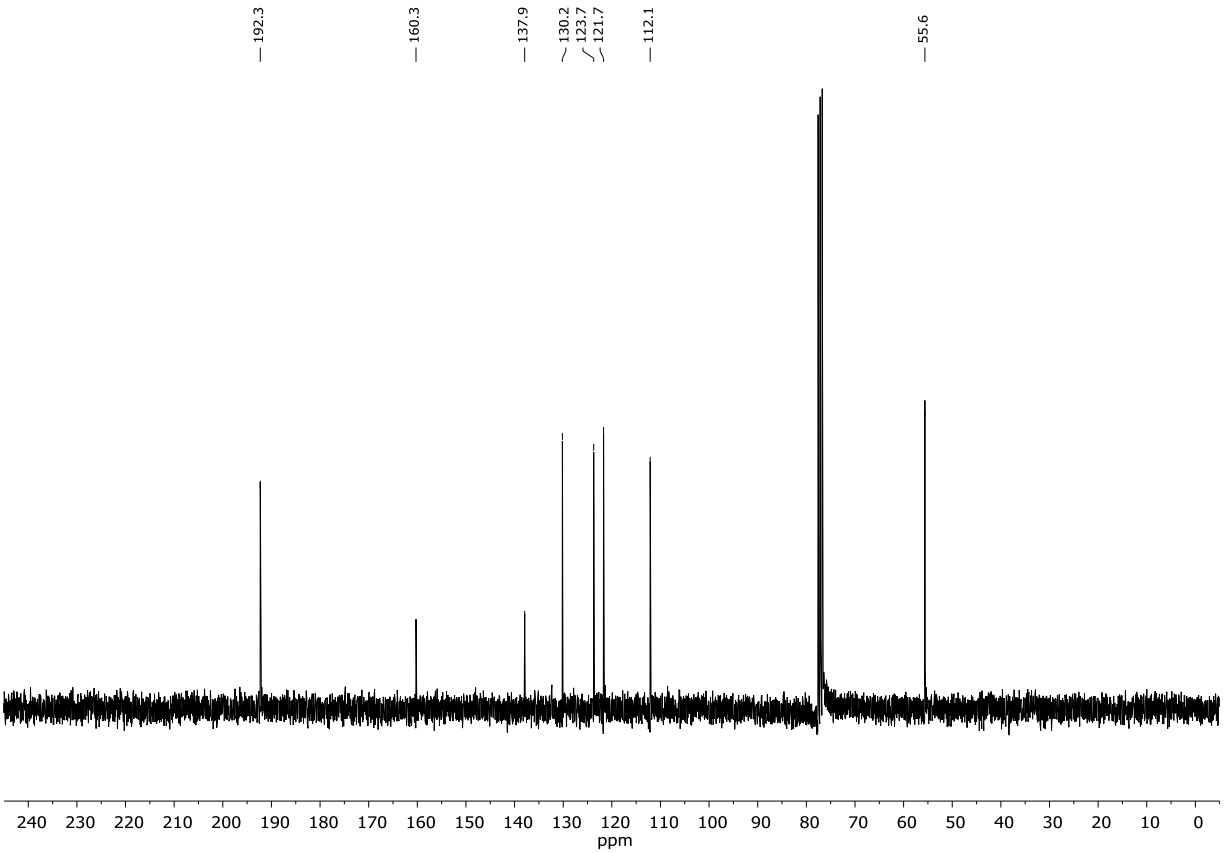
4-methoxybenzaldehyde (2a)





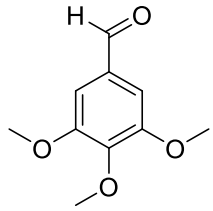
3-methoxybenzaldehyde (**2b**)

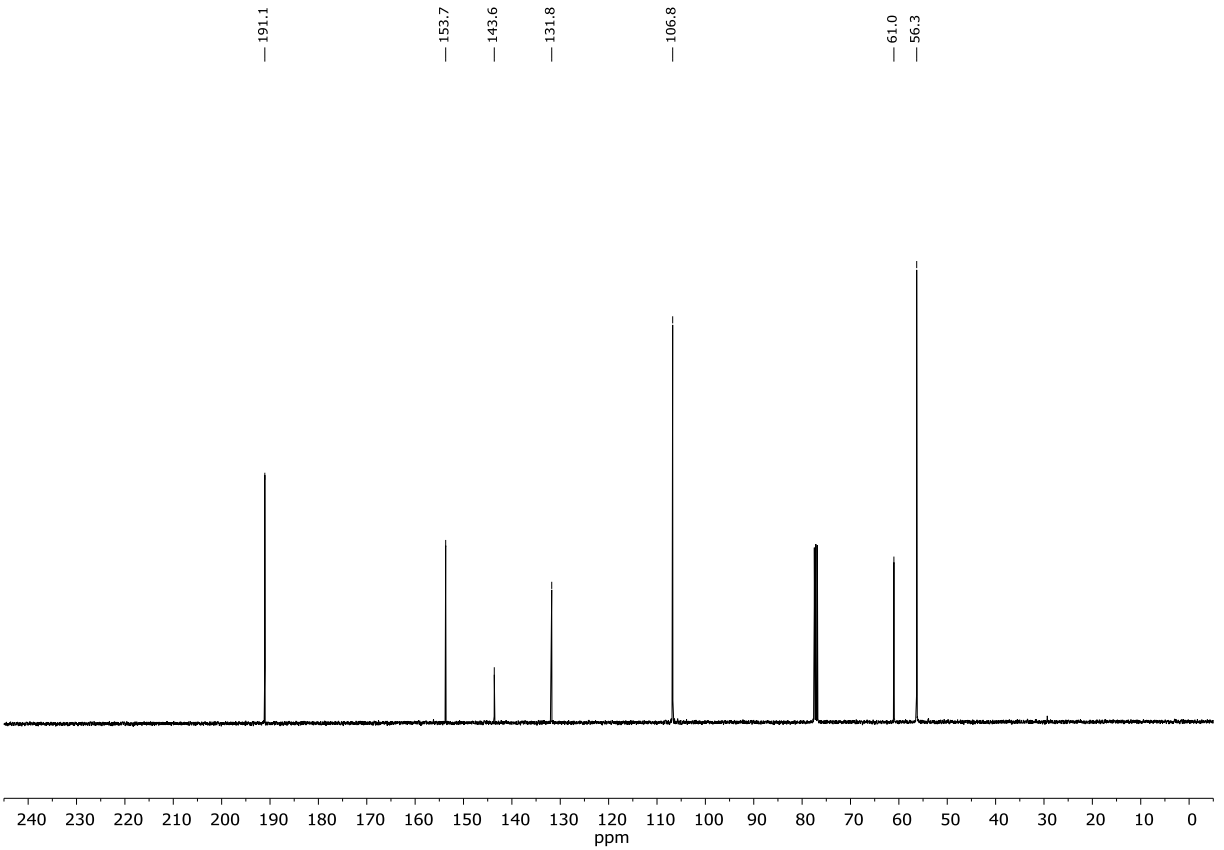




NMR solvent: $CDCl_3$

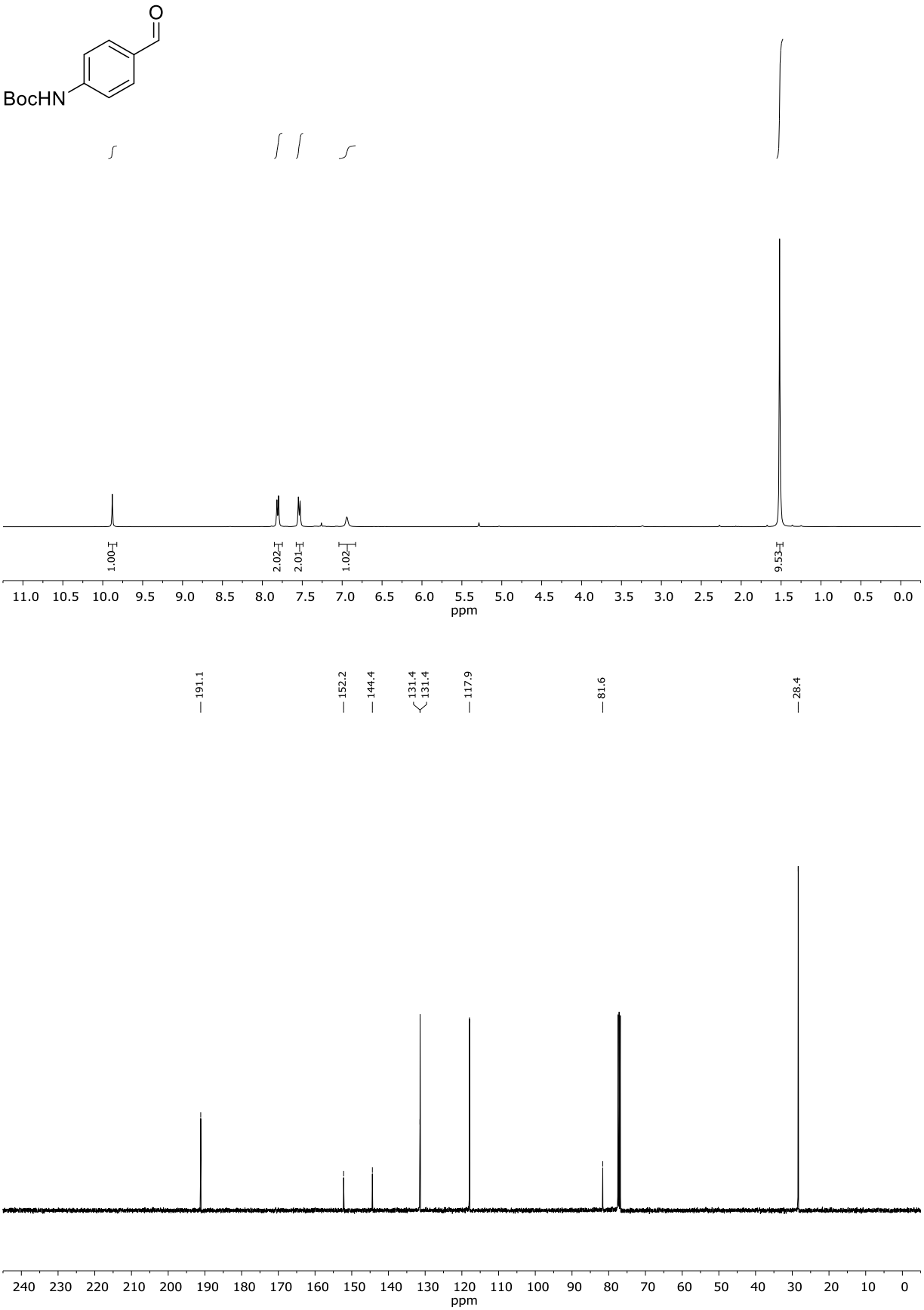
3,4,5-trimethoxybenzaldehyde (**2c**)





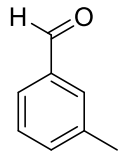
NMR solvent: $CDCl_3$

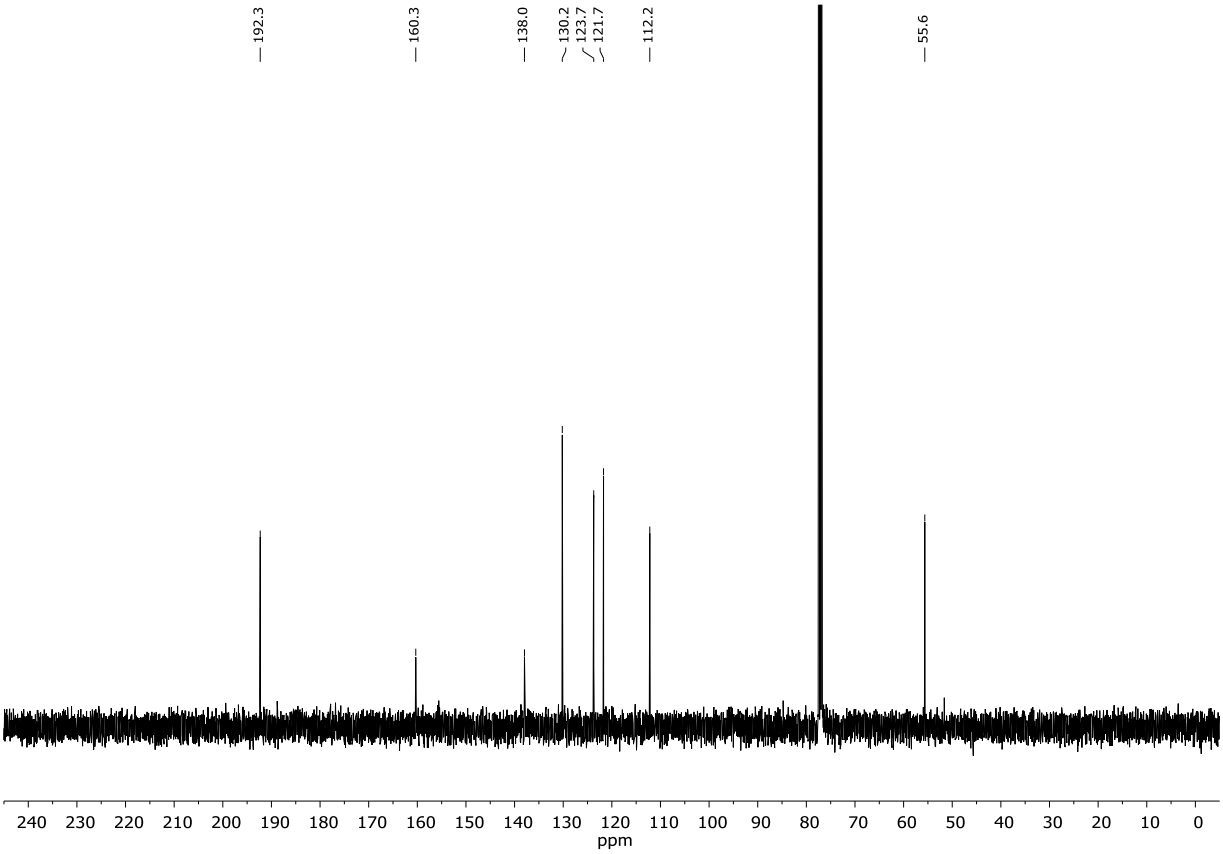
tert-butyl (4-formylphenyl)carbamate (2d)



NMR solvent: $CDCl_3$

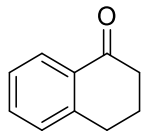
3-methylbenzaldehyde (2e)

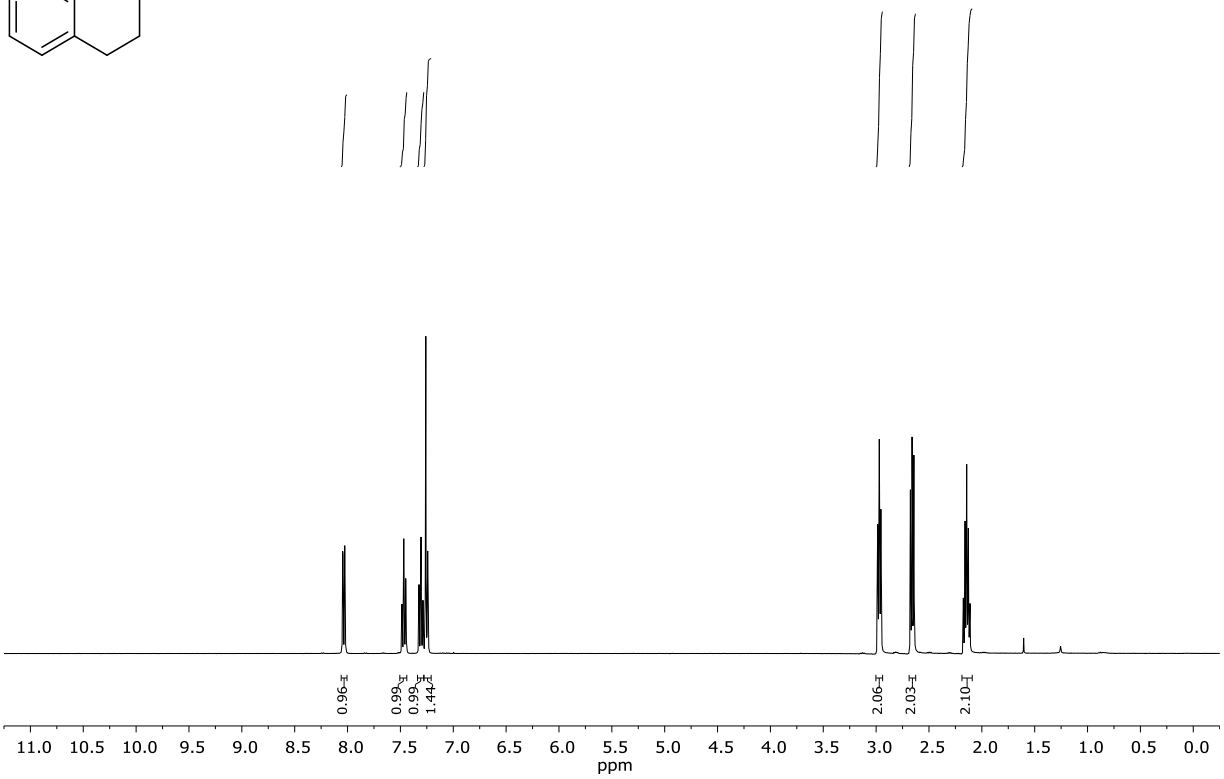


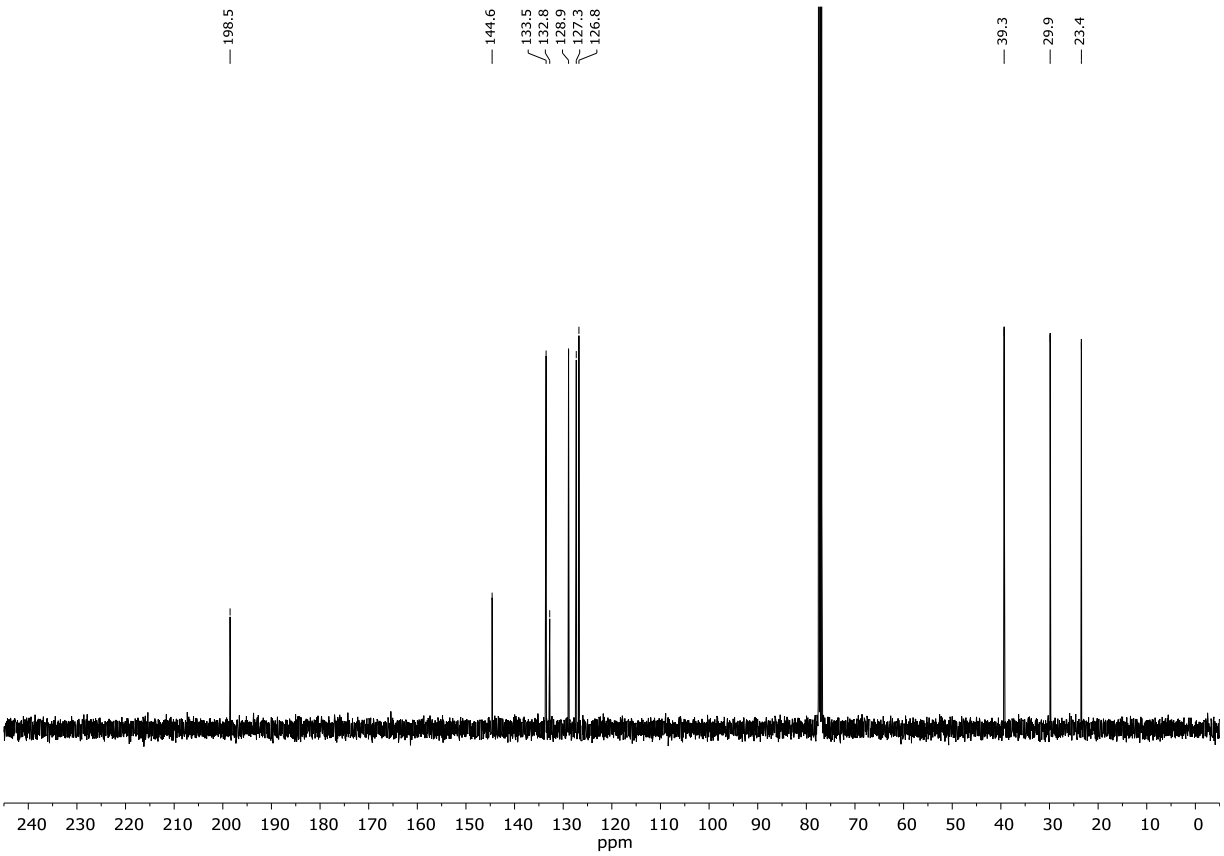


NMR solvent: $CDCl_3$

3,4-dihydronaphthalen-1(2H)-one (2h)

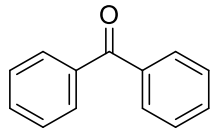


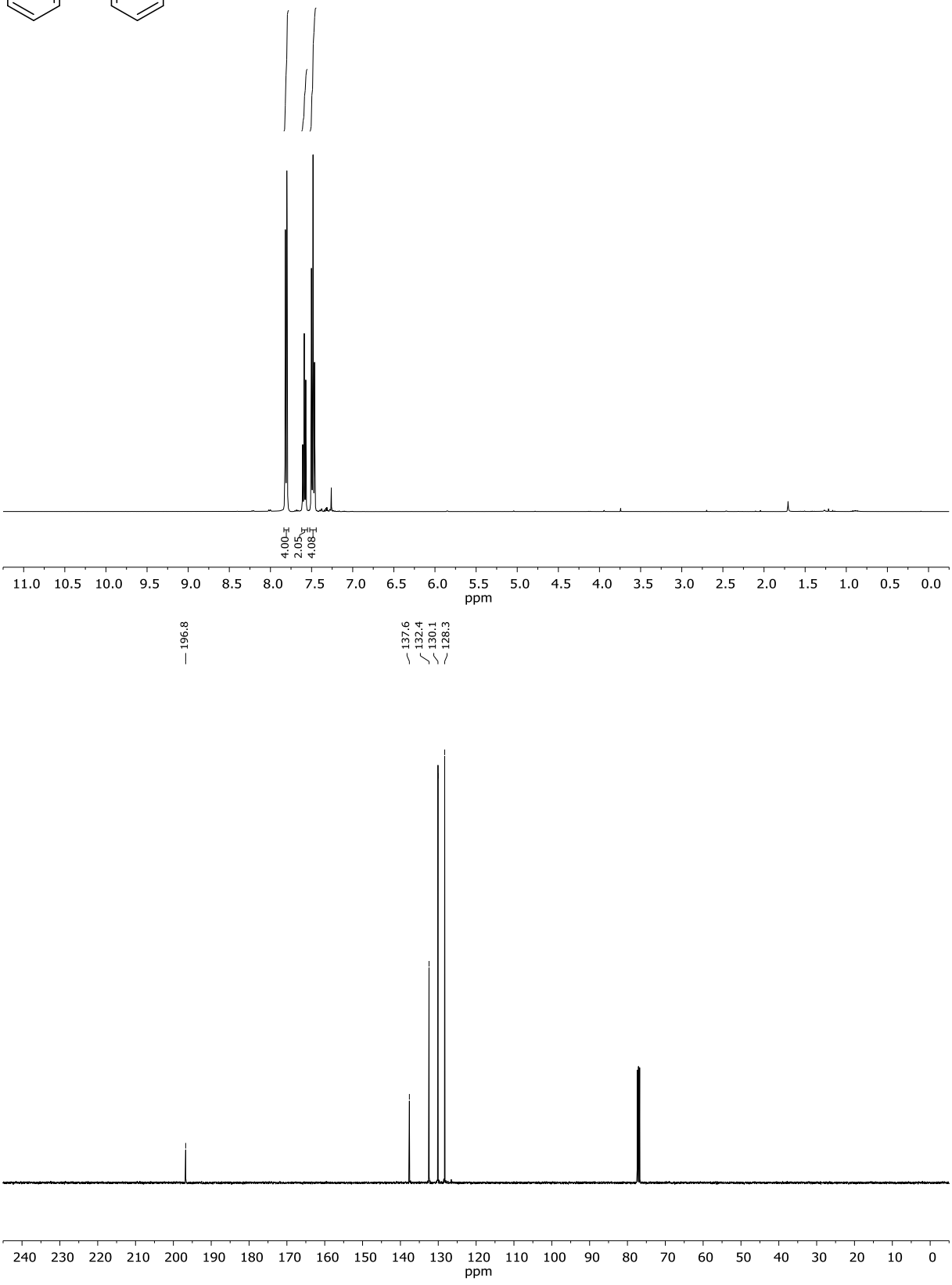




NMR solvent: $CDCl_3$

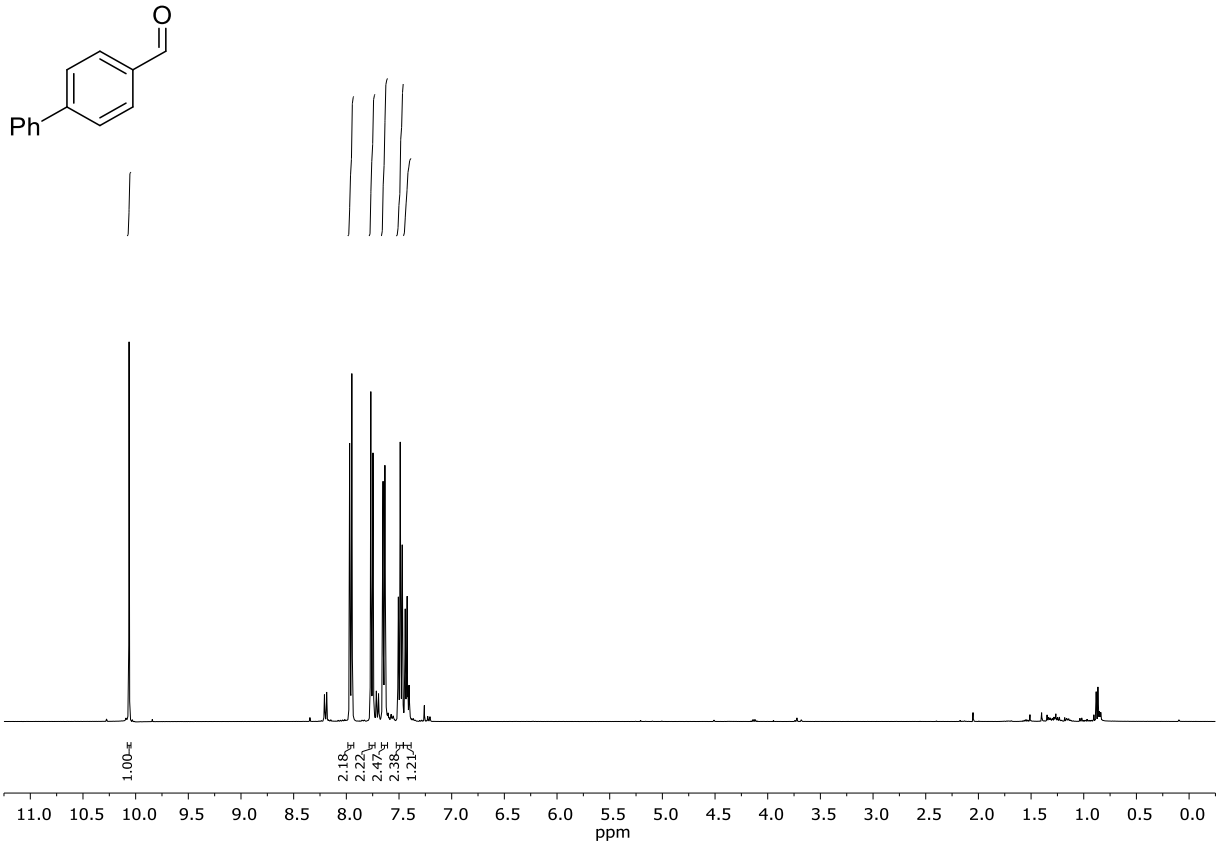
benzophenone (2i)

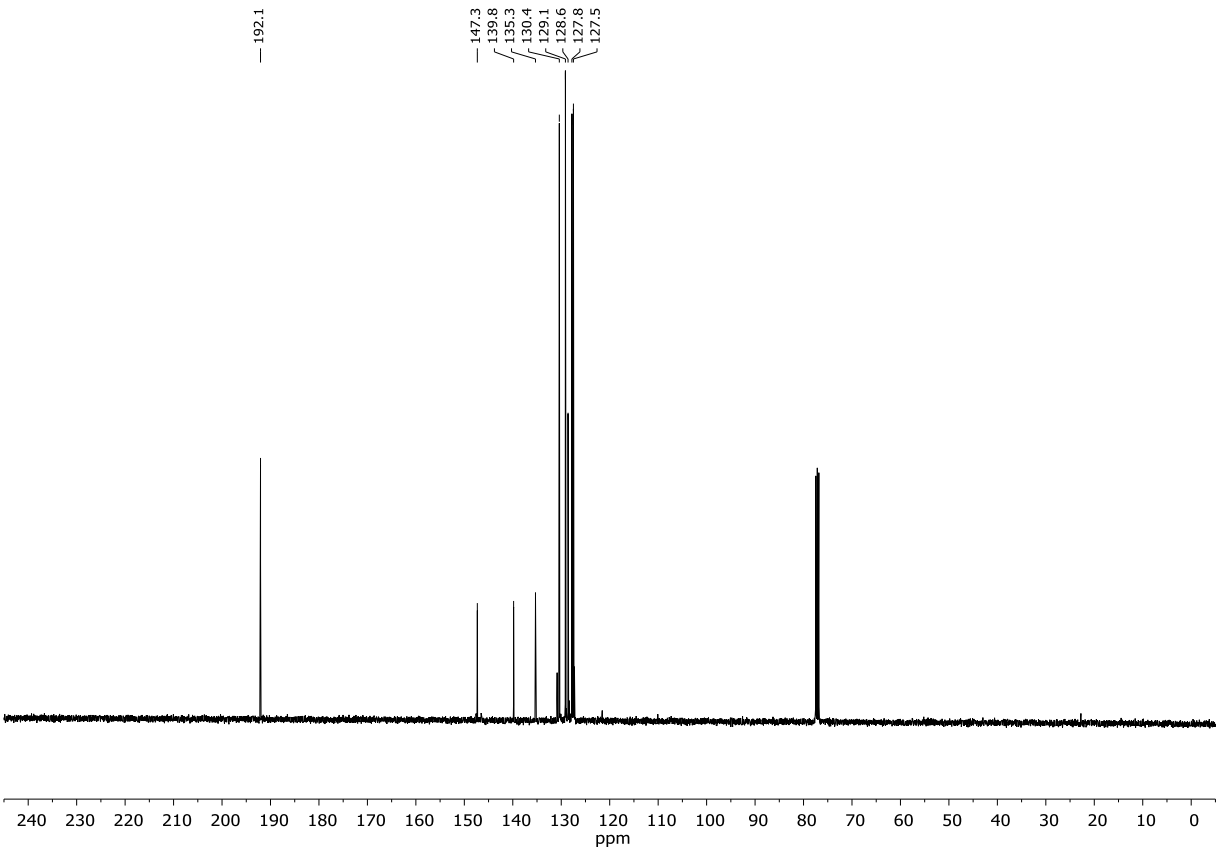




NMR solvent: $CDCl_3$

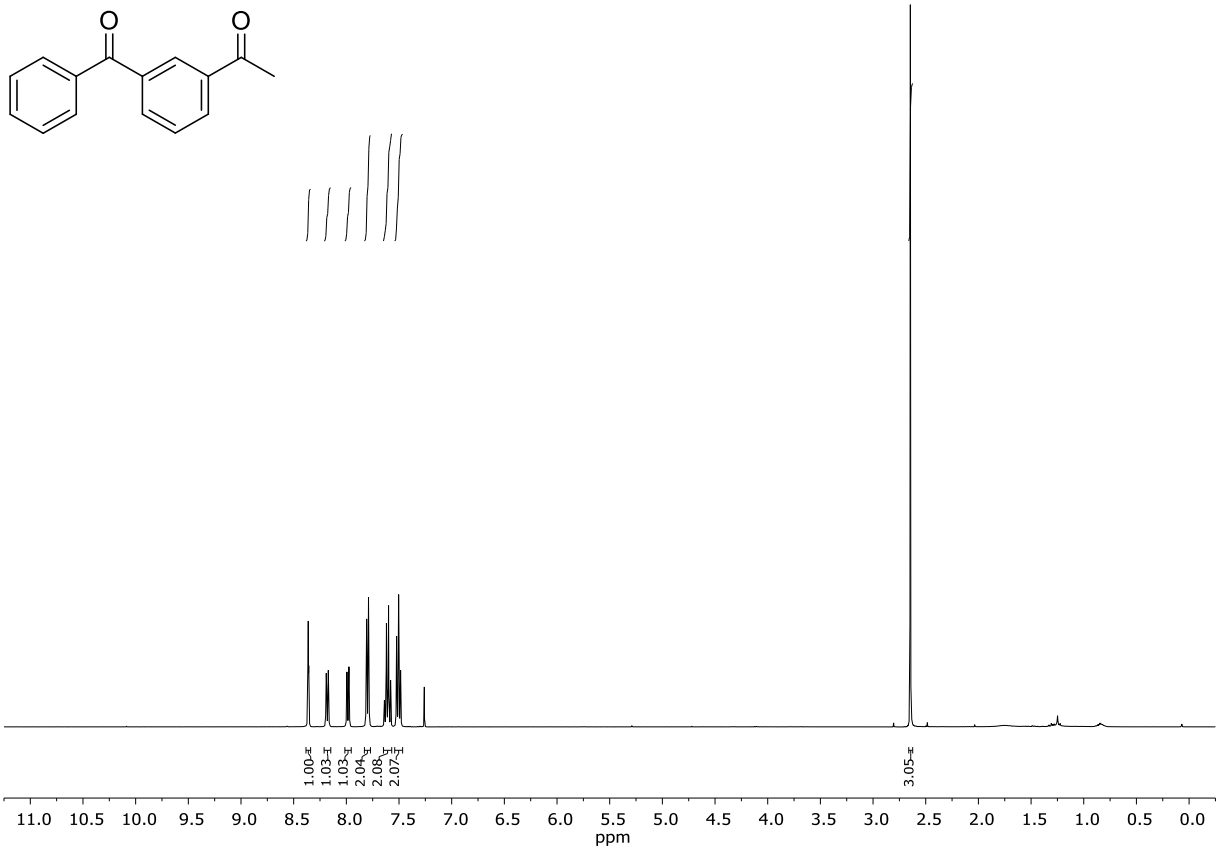
[1,1'-biphenyl]-4-carbaldehyde (2j)

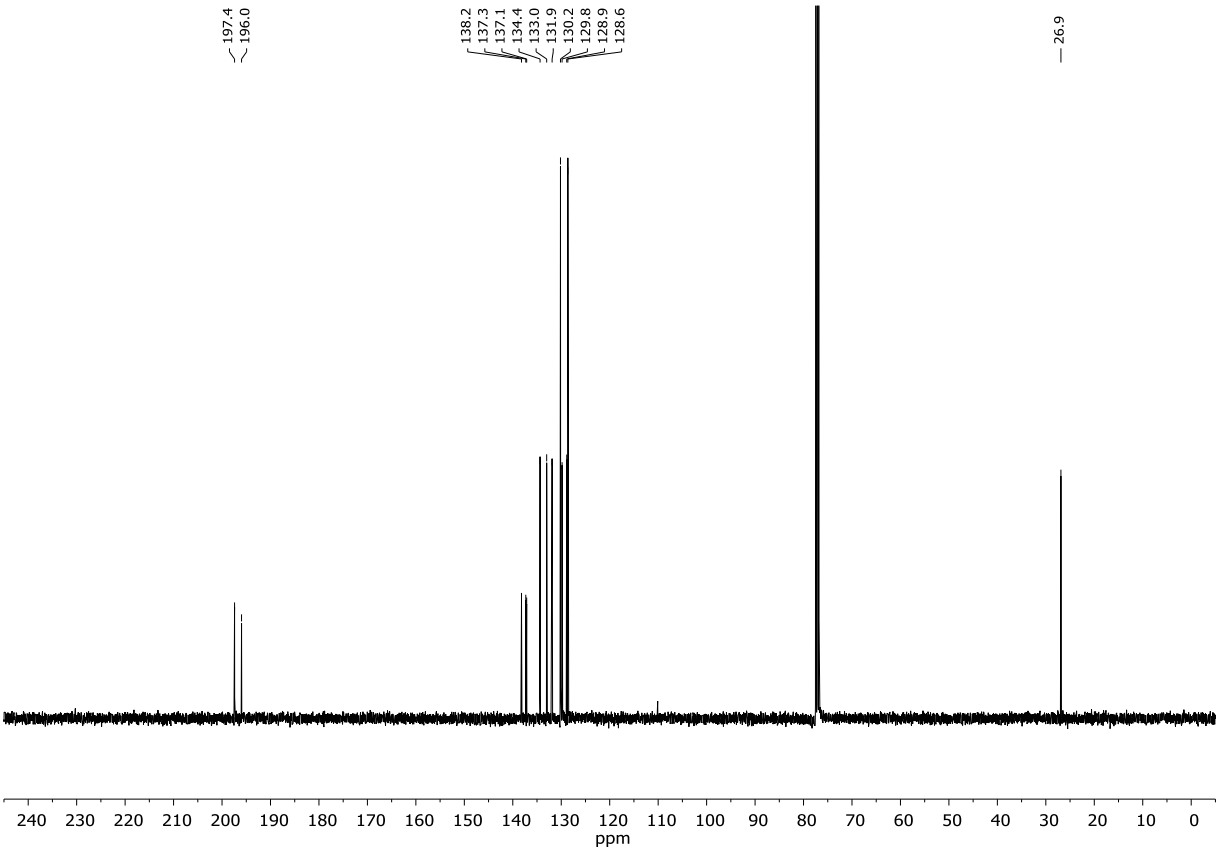




NMR solvent: $CDCl_3$

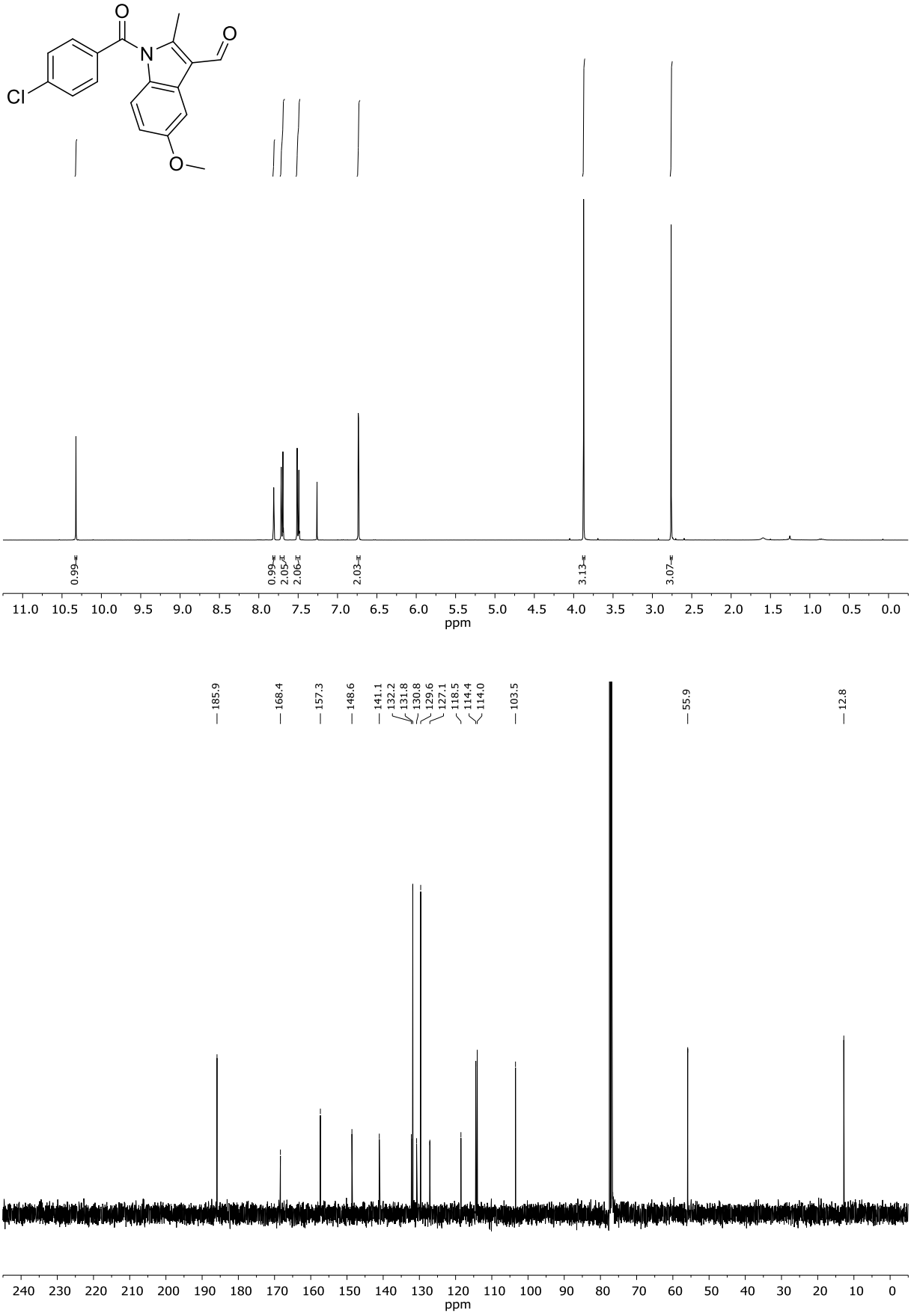
1-(3-benzoylphenyl)ethan-1-one (2k)





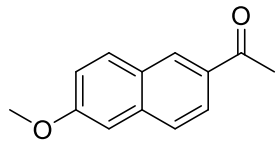
NMR solvent: $CDCl_3$

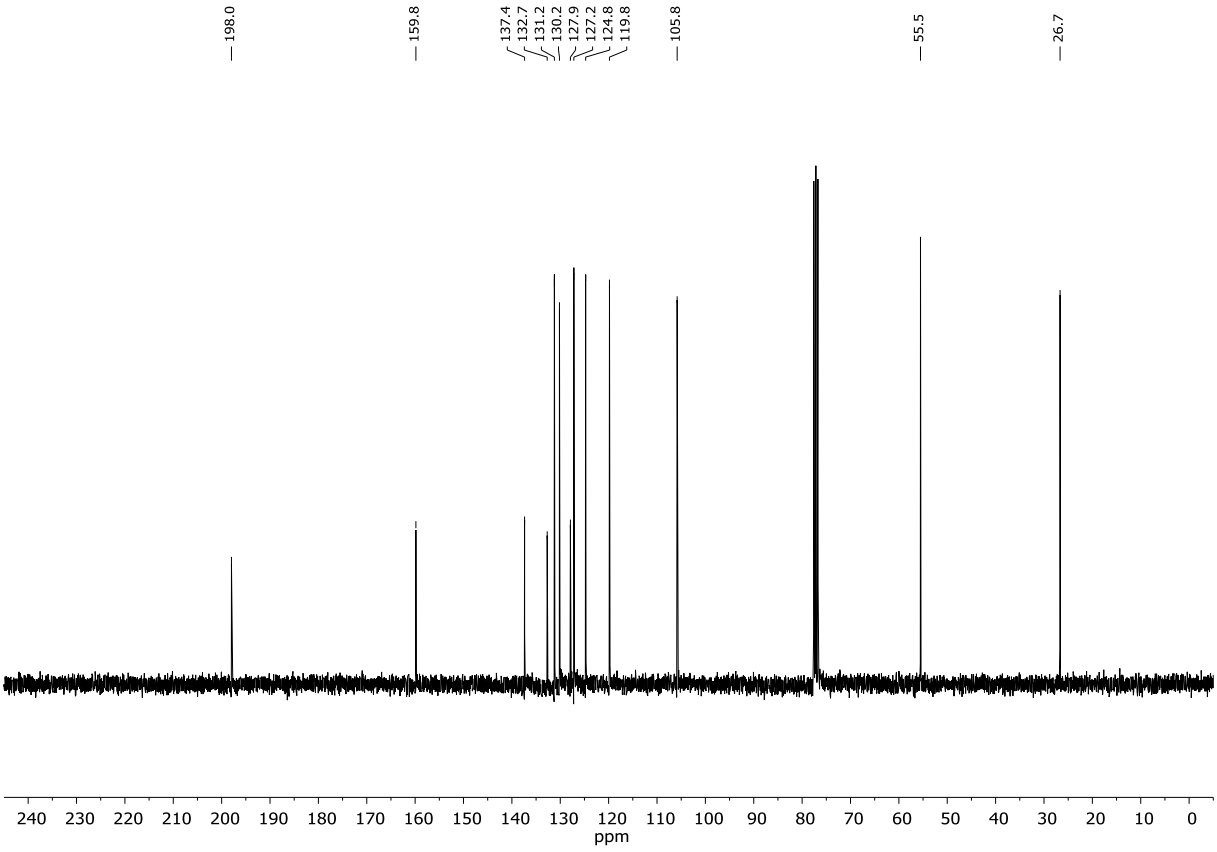
1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-carbaldehyde (2l)



NMR solvent: $CDCl_3$

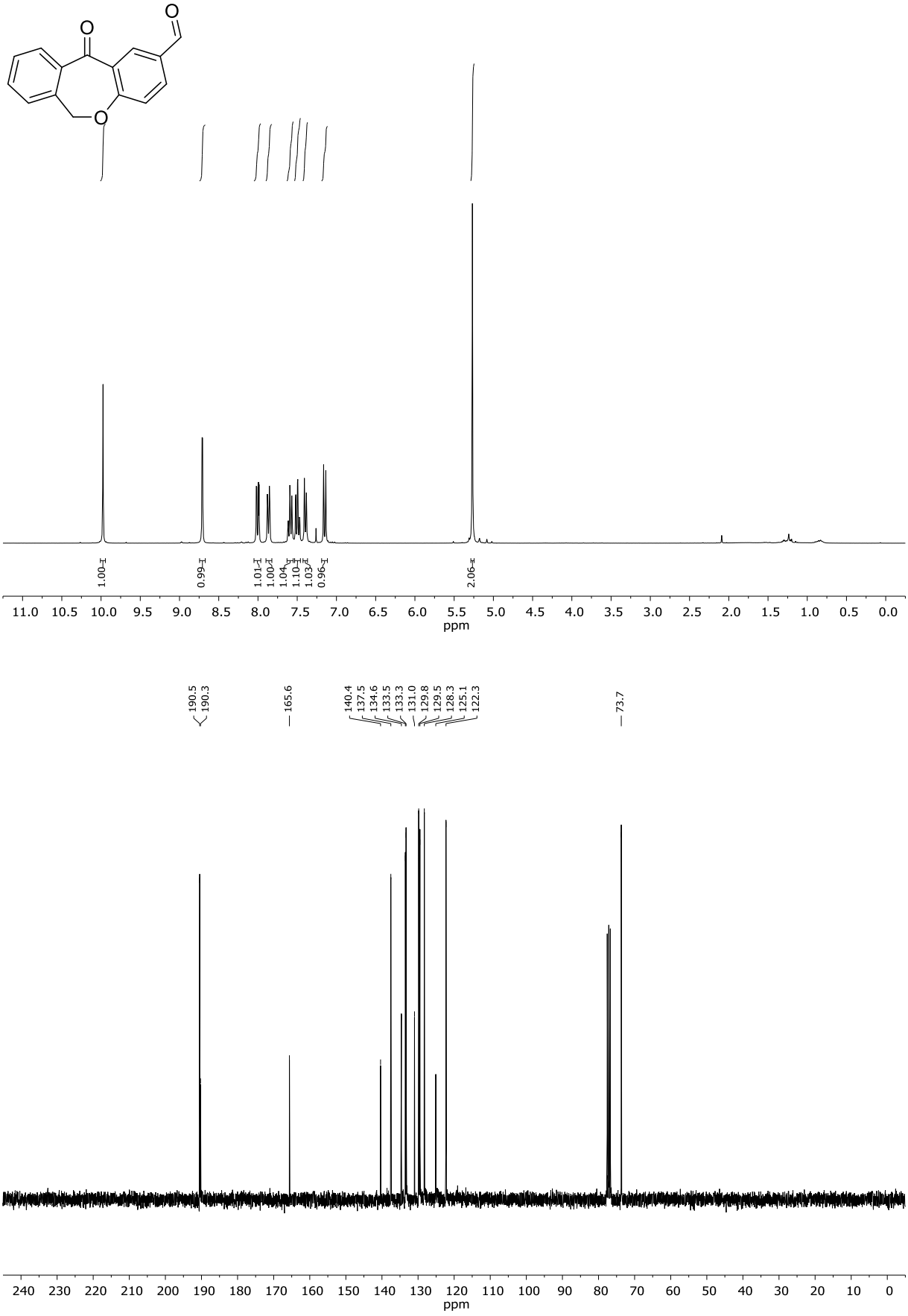
1-(6-methoxynaphthalen-2-yl)ethan-1-one/ naproxene (2m)





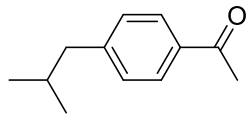
NMR solvent: $CDCl_3$

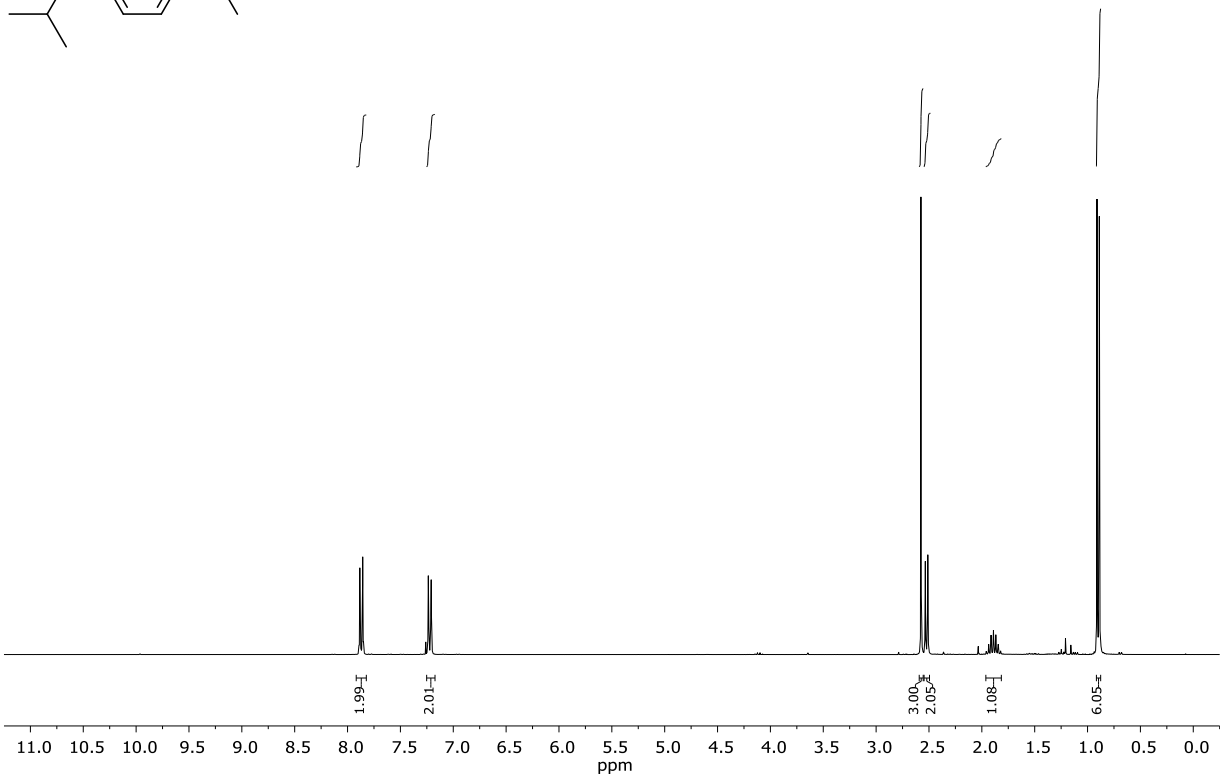
11-oxo-6,11-dihydrodibenzo[b,e]oxepine-2-carbaldehyde (2n)

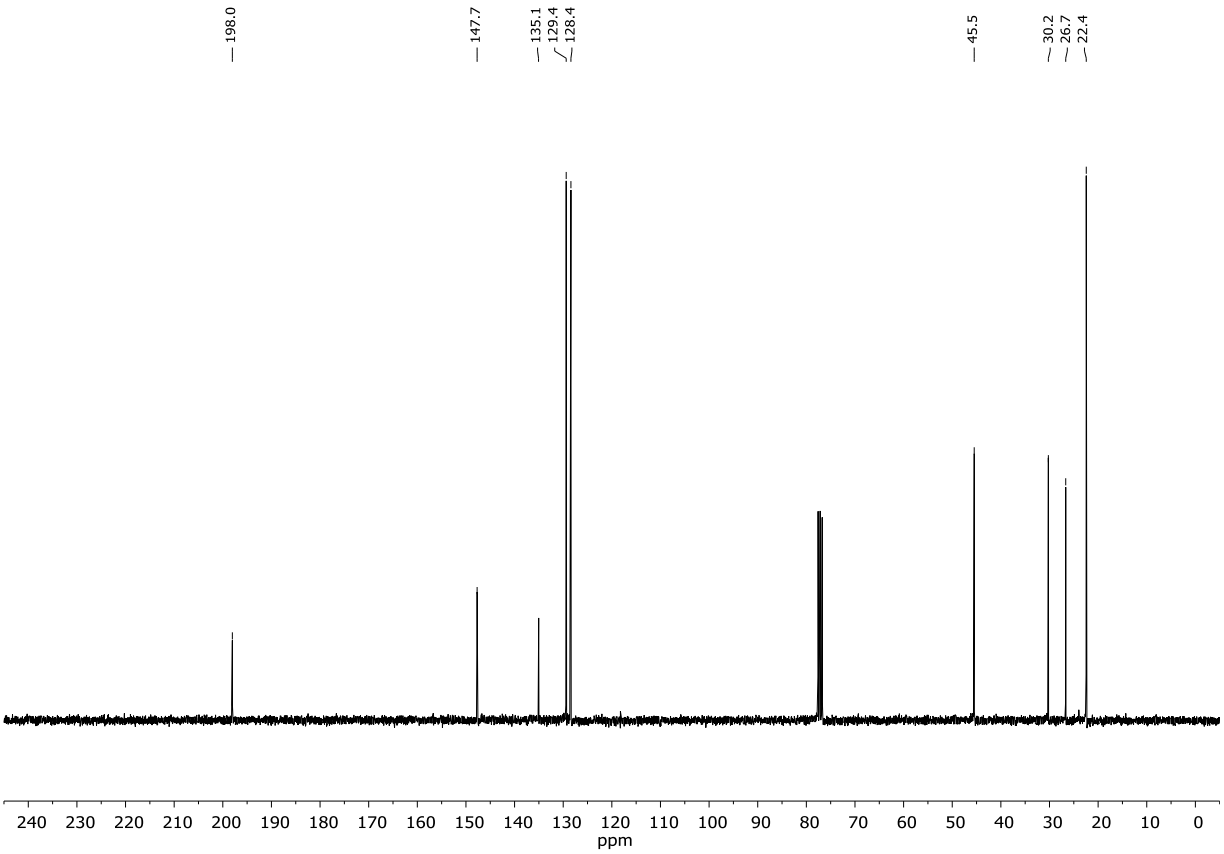


NMR solvent: $CDCl_3$

1-(4-isobutylphenyl)ethan-1-one (2o)

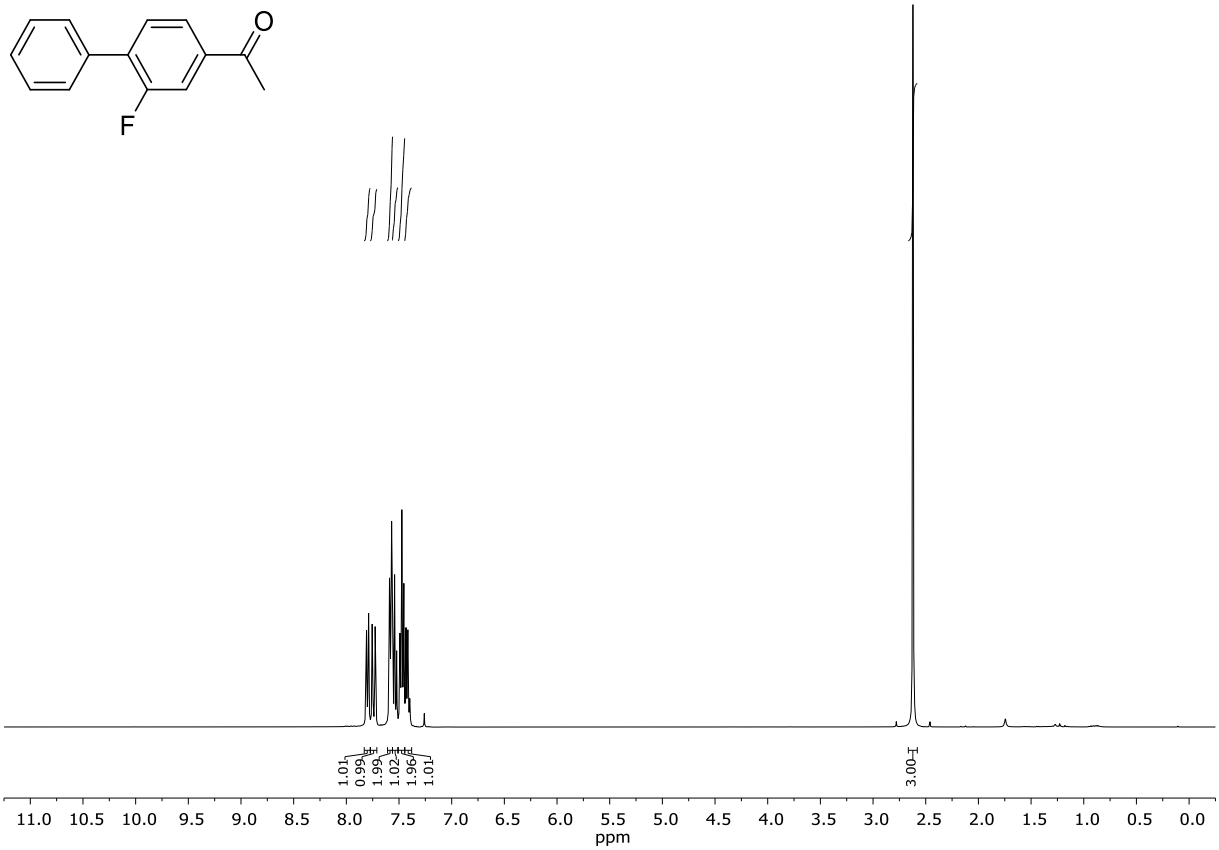


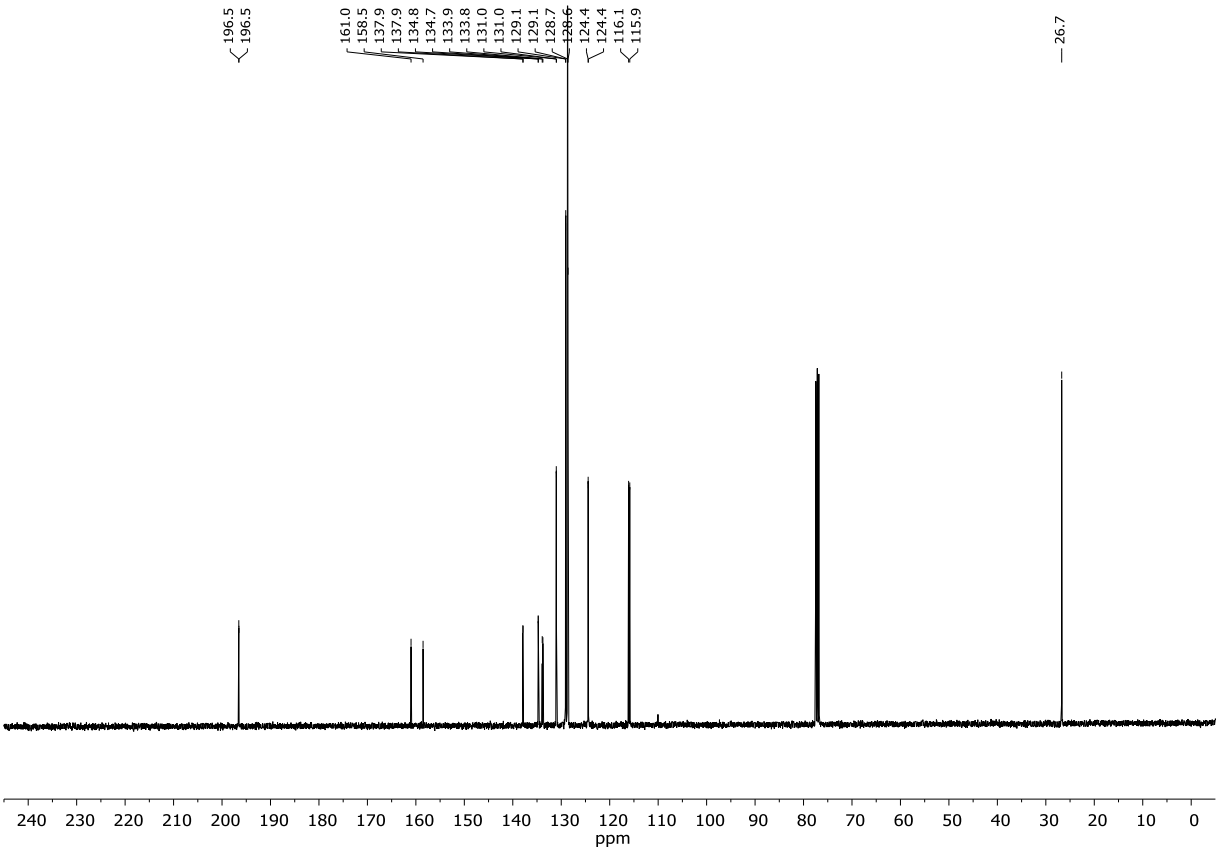




NMR solvent: $CDCl_3$

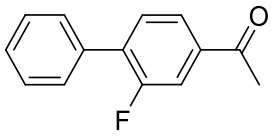
1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (2p)





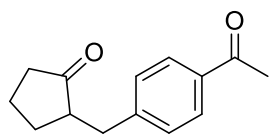
NMR solvent: $CDCl_3$

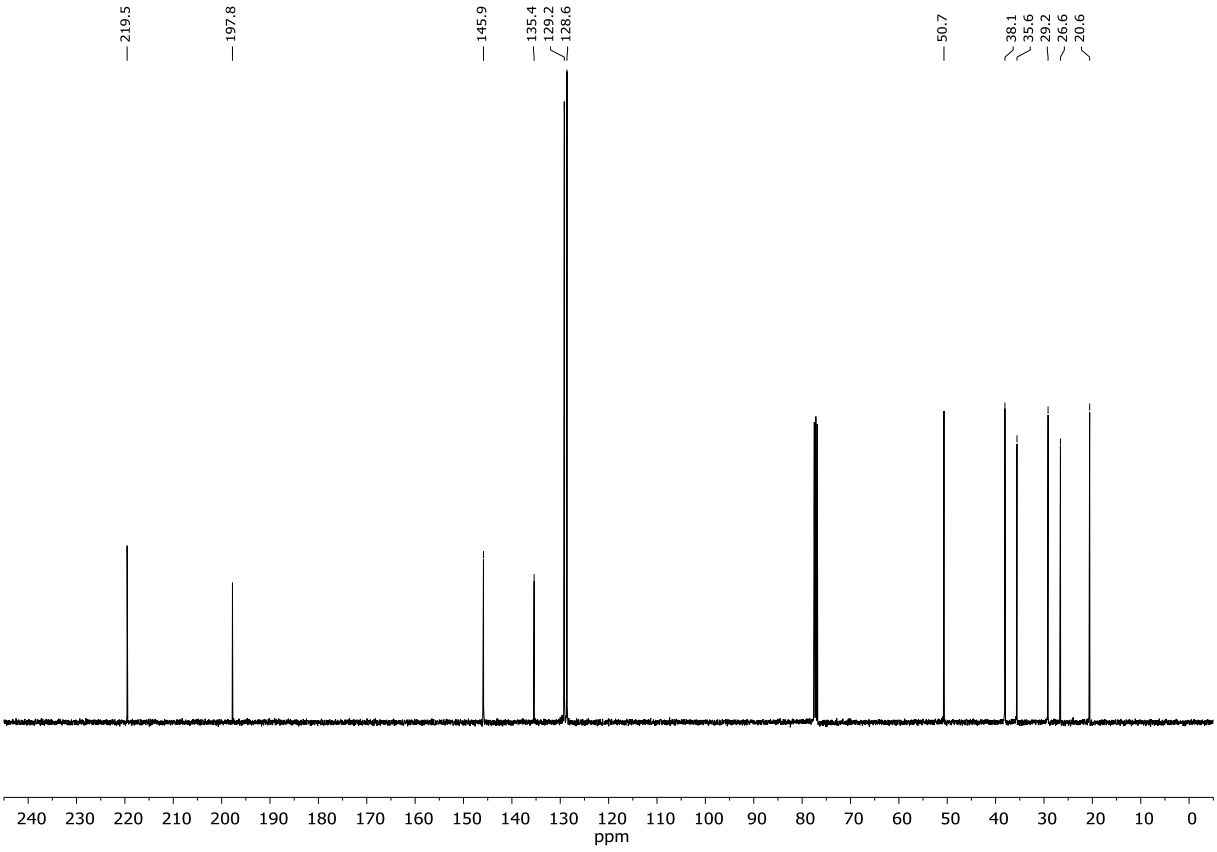
1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (2p)



NMR solvent: $CDCl_3$

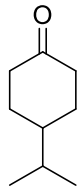
2-(4-acetylbenzyl)cyclopentan-1-one (2q)

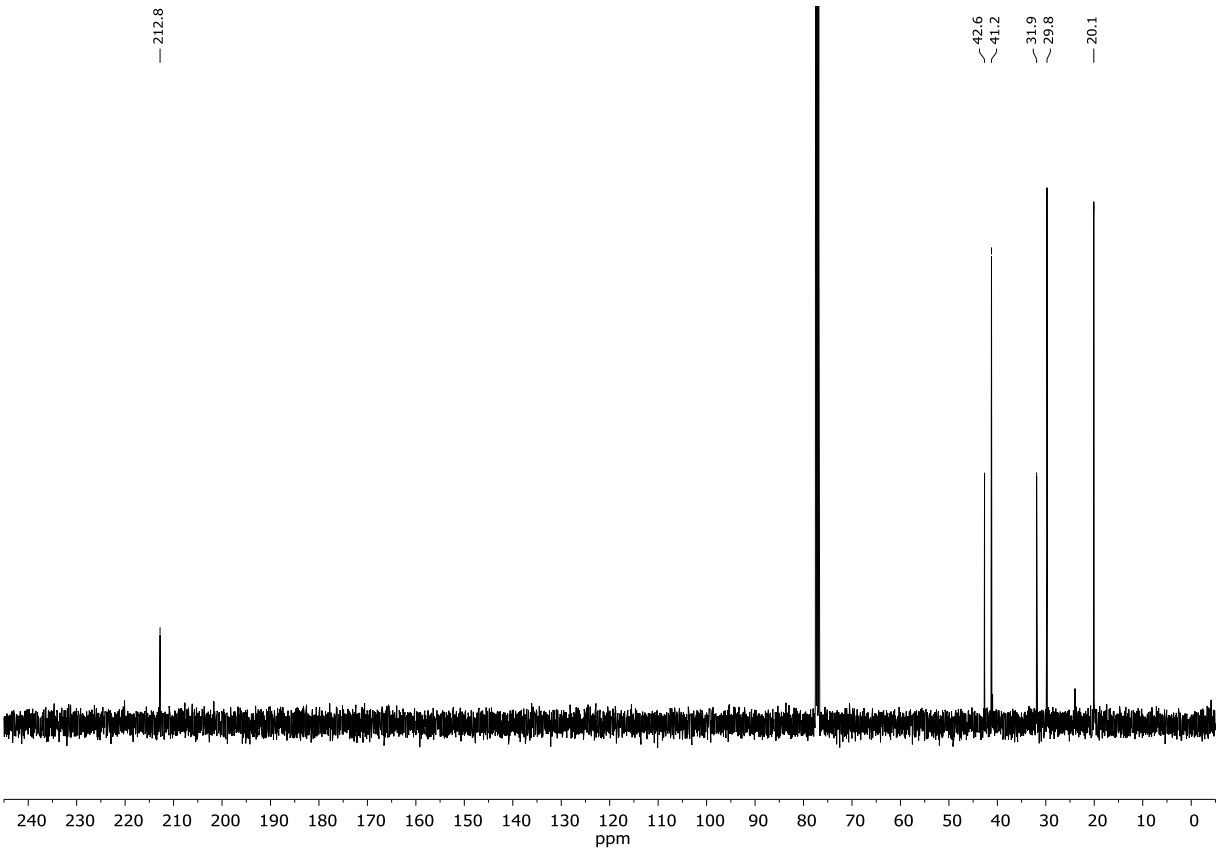




NMR solvent: $CDCl_3$

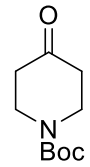
4-isopropylcyclohexan-1-one (2r)

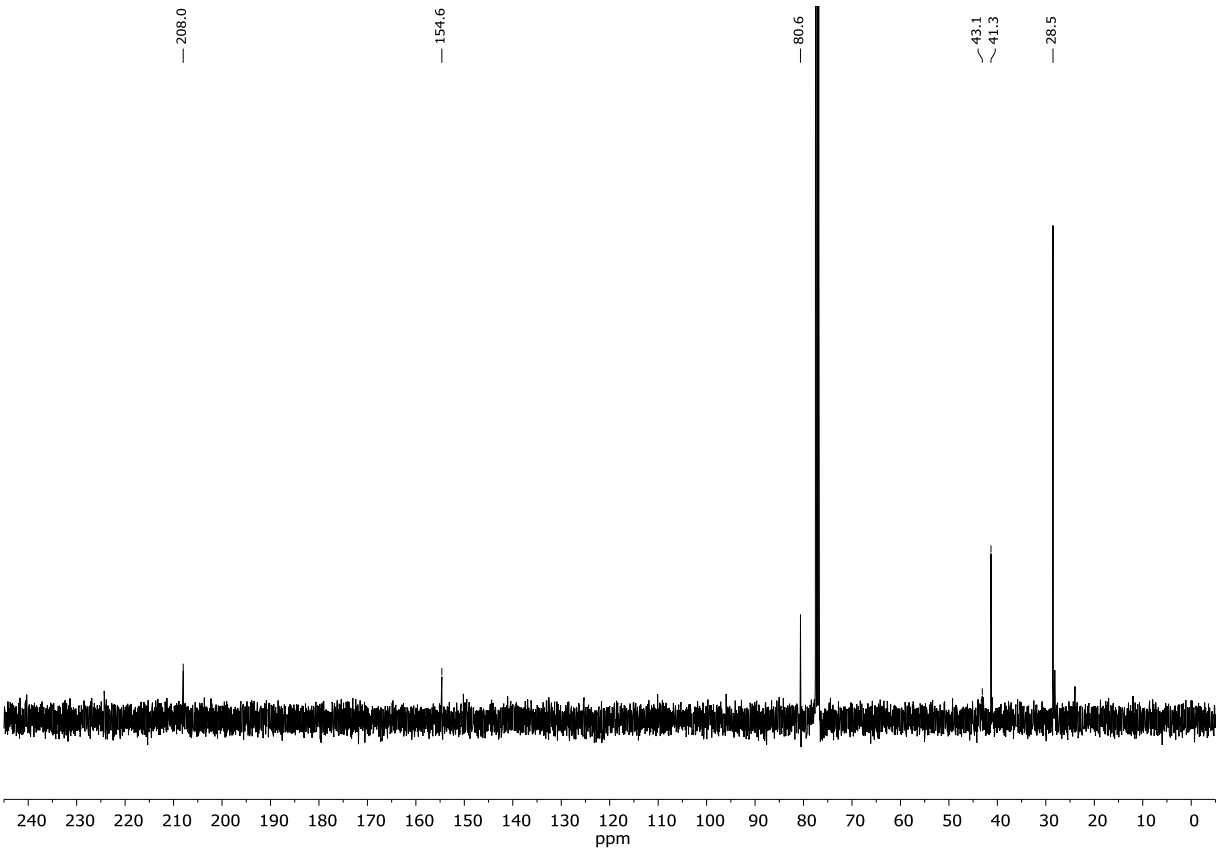




NMR solvent: $CDCl_3$

tert-butyl 4-oxopiperidine-1-carboxylate (2s)





NMR solvent: $CDCl_3$

9 Crystallographic Data

Compound	**Cu(4-MeOpa)$_4$(MeCN)$_2$ (3)**	**Cu(dmp)(4-MeOpa)$_2$ (4)**	**Isoxepac Derivative (2n)**	**Indometacin Derivative (2l)**
CCDC	2144482	2144474	2144480	2144485
Formula	$C_{20}H_{21}CuNO_6$	$C_{32}H_{30}CuN_2O_6$	$C_{15}H_{10}O_3$	$C_{18}H_{14}ClNO_3$
$D_{calc.}$/ g cm^{-3}	1.502	1.451	1.448	1.445
μ/mm^{-1}	1.930	1.529	0.830	2.377
Formula Weight	434.92	602.12	238.23	327.75
Colour	clear blue	clear green	clear colorless	clear colorless
Shape	plate-shaped	plate	plate-shaped	prism-shaped
Size/mm^3	0.23×0.15×0.06	0.15×0.10×0.05	0.17×0.11×0.06	0.09×0.08×0.08
T/K	123.01(10)	123.01(10)	122.97(10)	123.00(10)
Crystal System	triclinic	monoclinic	monoclinic	monoclinic
Space Group	*P*-1	*C*2/*c*	*C*2/*c*	*P*2$_1$/*c*
a/Å	9.8246(2)	25.6472(6)	13.7617(9)	16.06989(7)
b/Å	13.6030(3)	16.1411(4)	8.1050(4)	7.09422(3)
c/Å	14.54570(10)	13.7447(3)	19.5997(12)	26.42930(11)
α/°	83.192(2)	90	90	90
β/°	85.2690(10)	104.289(3)	91.551(6)	90.3024(4)
γ/°	88.081(2)	90	90	90
V/Å^3	1923.11(6)	5513.9(2)	2185.3(2)	3012.99(2)
Z	4	8	8	8
Z'	2	1	1	2
Wavelength/ Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	CuK$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.069	3.265	4.514	2.750
Θ_{max}/°	73.028	74.143	73.956	74.433
Measured Refl.	52324	14926	11611	66058

Independent Refl.	7274	5395	2140	6106
Reflections with I > 2(I)	5785	4303	1916	5835
R_{int}	0.0848	0.0270	0.0445	0.0186
Parameters	511	374	163	419
Restraints	0	0	0	0
Largest Peak	0.607	0.941	0.310	0.263
Deepest Hole	-1.121	-0.435	-0.260	-0.395
GooF	1.126	1.018	1.046	1.048
wR_2 (all data)	0.1544	0.1061	0.1339	0.0790
wR_2	0.1461	0.0974	0.1311	0.0782
R_1 (all data)	0.0676	0.0506	0.0568	0.0297
R_1	0.0536	0.0380	0.0525	0.0286
Creation Method				
Solution		Olex2 1.2-alpha		
Refinement		(compiled 2018.07.26 svn.r3523 for OlexSys, GUI svn.r5532)		

10 EPR Measurements

10.1 General Information

Continuous-wave (CW) electron paramagnetic resonance (EPR) experiments were carried out in acetonitrile solutions on a Bruker EMX Spectrometer (X-Band, 9-10 GHz) equipped with an ER 083 (200/60) power source electromagnet (0-6000 G). For the measurements, an ER 4104 OR/9009 resonant cavity with a resonance frequency of 9.66 GHz was used. Samples were measured in glass pipettes, which were evacuated and flushed with dry N_2 several times before being filled with 0.3 mL solution. Solvents were degassed by three freeze-pump-thaw cycles and stored under dry N_2 for no more than one week. Between preparation and the first obtained spectrum 10-15 min went by. To exclude light, samples were covered with tin foil during this time.

Irradiation during measurements was performed with a Luminus SST-10 (3 W, 720 mA, λmax = 365 nm) LED and by the use of an optical fiber cable FP1500URT (0.50 NA, 300-1200 nm, 1500 µm, multimode, end A SMA, end B flat cleave).

For measurements under oxygen atmosphere the samples were connected to a balloon containing oxygen.

EPR spectra were obtained as a first order derivative plot. Raw data were exported in the ASCII file format and processed with Origin 2019b (Version 9.6.5.169). All spectra are baseline and solvent corrected. For quantitative comparisons the spectra were integrated twice.

For all measurements a stock solution of 2 mL was prepared. All measurements were done in acetonitrile unless stated otherwise.

10.2 Comparison of 3 and 4

Comparison of the EPR spectra of the Paddlewheel complex **3** and monomeric complex **4** were done using the following measurement parameters.

Table S3: Parameters for Comparision of **3** and **4**.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
3	9.325401 GHz	62.10 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
4	9.317844 GHz	60.61 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

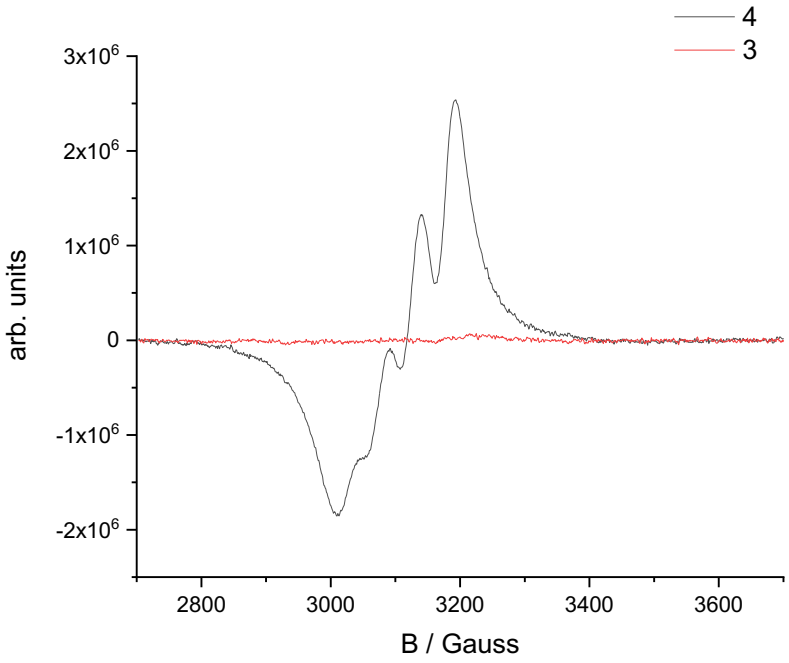


Figure S7: Cu^{II}-complex **4** (12.5 mmol/L) or **3** (6.25 mmol/L) formed *in situ* in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) from Copper(II)-carboxylate at room temperature (25 °C).

10.3 Water Titration Experiment

A water titration experiment was done using the following measurement parameters:

Table S4: Parameters for Water Titration Experiment.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
0.2 Vol%	9.327895 GHz	59.82 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
2.2 Vol%	9.317844 GHz	60.61 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
5.4 Vol%	9.327079 GHz	59.82 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
10.3 Vol%	9.327531 GHz	60.06 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
18.7 Vol%	9.327444 GHz	60.21 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

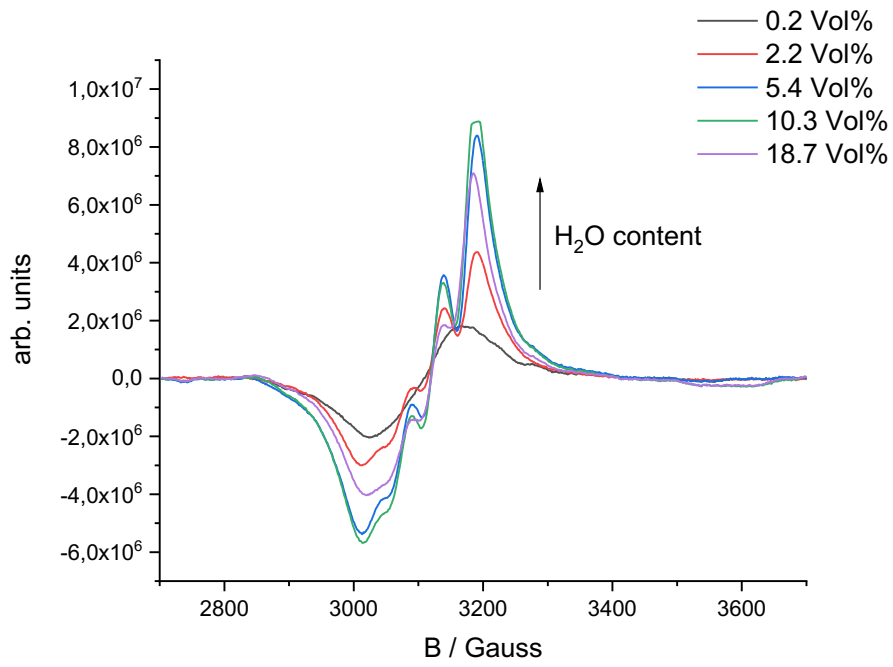


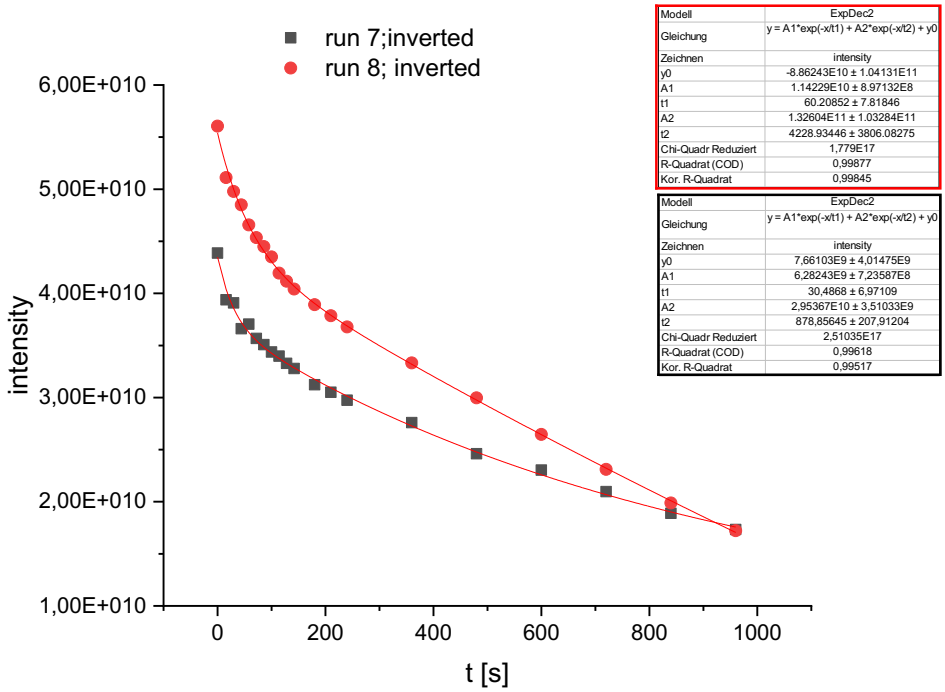
Figure S8: Cu^{II}-complex **4** (12.5 mmol/L) formed in situ in MeCN (2.0 mLat room temperature (25 °C). Water: 0.2 Vol% (4.5 µL), 2.2 Vol% (45 µL), 5.4 Vol% (115 µL), 10.3 Vol% (230 µL), 18.7 Vol% (461 µL).

10.4 Reaction Kinetic Measurements

The kinetic measurements were done using the following measurement parameters.

Table S5: Parameters for Reaction Kinetic Measurements.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Run7	9.303960 GHz	63.32 mW	25 G	21.0 ms	20.48 ms	2.0×10^4	512
Run8	9.304450 GHz	63.40 mW	25 G	21.0 ms	20.48 ms	2.0×10^4	512



Modell	ExpDec2
Gleichung	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Zeichnen	intensity
y0	-8.86243E10 ± 1.04131E11
A1	1.14229E10 ± 8.97132E8
t1	60.20852 ± 7.81846
A2	1.32604E11 ± 1.03284E11
t2	4228.93446 ± 3806.08275
Chi-Quadr Reduziert	1,779E17
R-Quadrat (COD)	0,99877
Kor. R-Quadrat	0,99845

Modell	ExpDec2
Gleichung	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Zeichnen	intensity
y0	7,66103E9 ± 4,01475E9
A1	6,28243E9 ± 7,23587E8
t1	30,4868 ± 6,97109
A2	2,95367E10 ± 3,51033E9
t2	878,85645 ± 207,91204
Chi-Quadr Reduziert	2,51035E17
R-Quadrat (COD)	0,99618
Kor. R-Quadrat	0,99517

Figure S9: 1a (125 mmol/L), Cu^{II}-complex **4** (12.5 mmol/L) in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) at room temperature (25 °C). Irradiation at 365 nm with a radiant power of 30 mW under O_2 atmosphere.

For the determination of k_1 and k_2, the average of $1/t_1$ and $1/t_2$ was used.

$k_1 = 0.022 \pm 0.003\ s^{-1}$

$k_2 = 4.982 \times 10^{-4} \pm 1.723 \times 10^{-4}\ s^{-1}$

10.5 Radical Trapping Experiments

Radical trapping experiments were done using the following measurement parameters.

Table S6: Parameters for Radical Trapping Experiments.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
PBN1	9.322388 GHz	62.59 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024
PBN2	9.304027 GHz	62.27 mW	3 G	82.0 ms	81.92 ms	2.0×10^4	512
TEMPO	9.305853 GHz	61.86 mW	25 G	83.0 ms	81.92 ms	2.0×10^4	1024

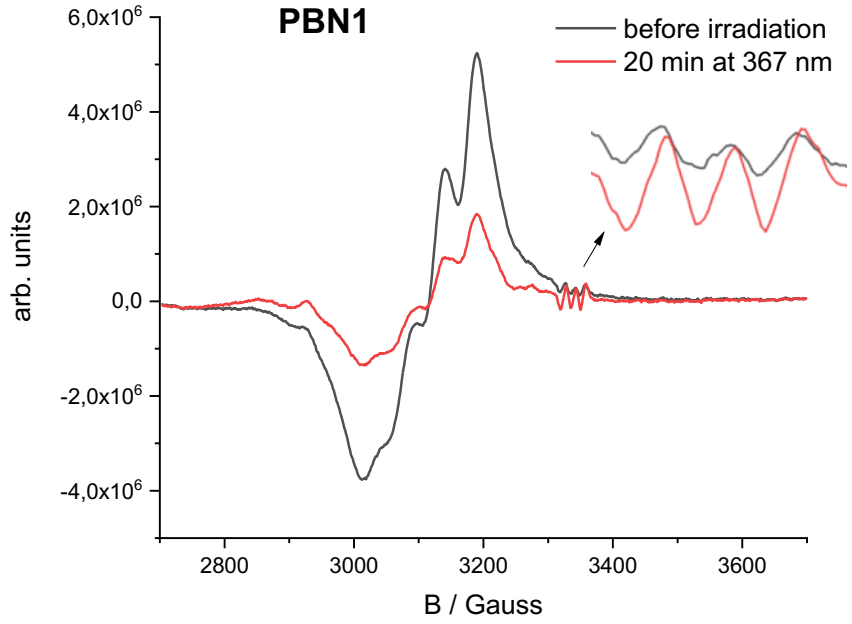


Figure S10: *N*-tert-Butyl-α-phenylnitrone (PBN) (150 mmol/L, 1.2 equiv) **1a** (125 mmol/L, 1 equiv), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 equiv) in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW.

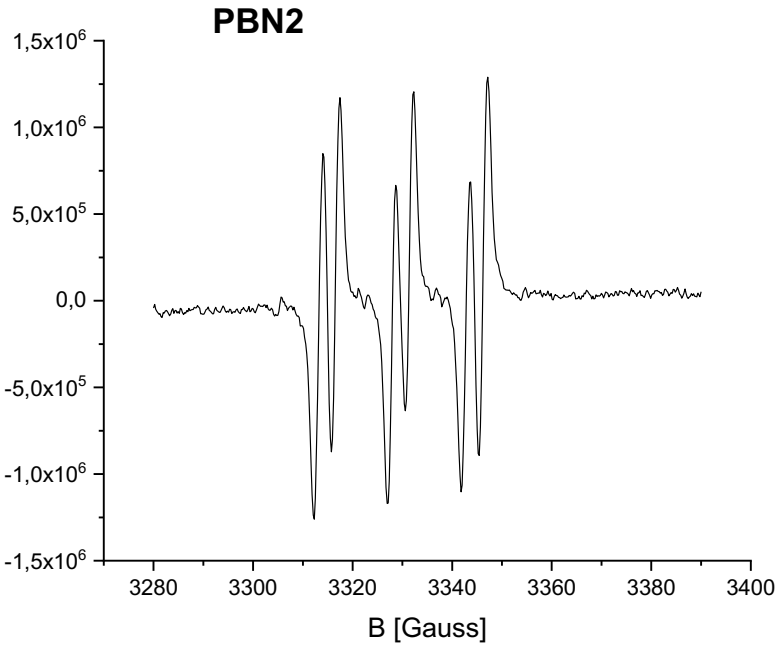


Figure S11: *N*-tert-Butyl-α-phenylnitrone (PBN) (150 mmol/L, 1.2 equiv) **1a** (125 mmol/L, 1 equiv), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 equiv) in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW for 15 min. The sum of 3 measurements is plotted.

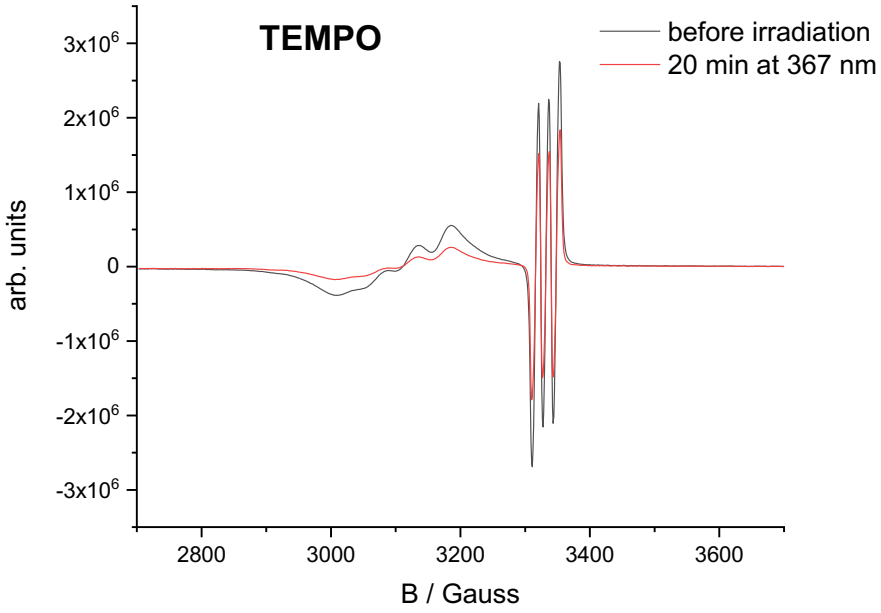


Figure S12: TEMPO (12.5 mmol/L, 0.1 equiv), **1a** (125 mmol/L, 1 equiv), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 equiv) in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) at room temperature (25 °C). Irradiation at 367 nm with a radiant power of 30 mW.

10.6 Light-on-off-cycle Experiment

For the light-on-off-cycle experiment the signal intensity of PBN-R is being measured every 20 s. The following measurement parameters were used.

Table S7: Parameters for Light-on-off-cycle Experiment.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
PBN	9.303935 GHz	62.27 mW	25 G	41.0 ms	40.96 ms	2.0×10^4	256

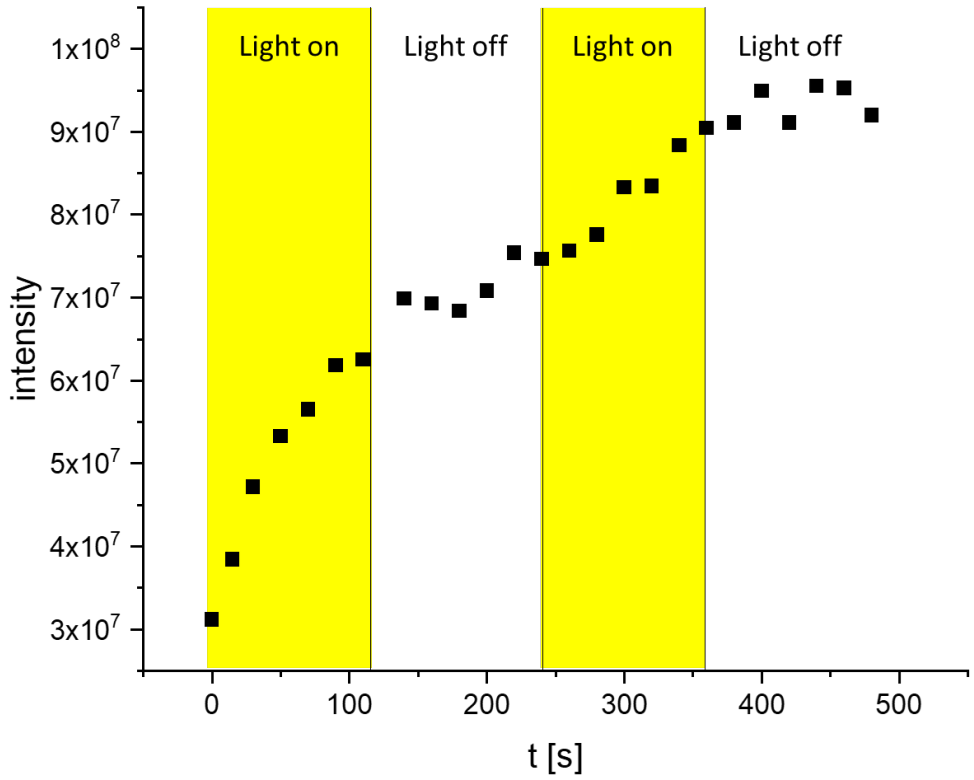


Figure S13: *N*-tert-Butyl-α-phenylnitrone (150 mmol/L, 1.2 equiv) **1a** (125 mmol/L, 1 equiv), Cu^{II}-complex **4** (12.5 mmol/L, 0.1 equiv) in MeCN (2.0 mL), water (45 µL, 2.2 Vol%) at room temperature (25 °C). Irradiation at 365 nm with a radiant power of 30 mW.

10.7 Measurements at 78 K

Measurements of complex **4** in liquid N_2 were done using the following parameters.

Table S8: Parameters for Measurements at 78 K.

Spectrum	Resonance Frequency	Microwave Power	Modulation Amplitude	Conversion Time	Time Constant	Receiver gain	Resolution
Acetonitrile	9.319510 GHz	18.75 mW	25 G	82.0 ms	81.92 ms	2.0×10^1	1024
Methanol	9.320521 GHz	18.71 mW	25 G	82.0 ms	81.92 ms	2.0×10^4	1024

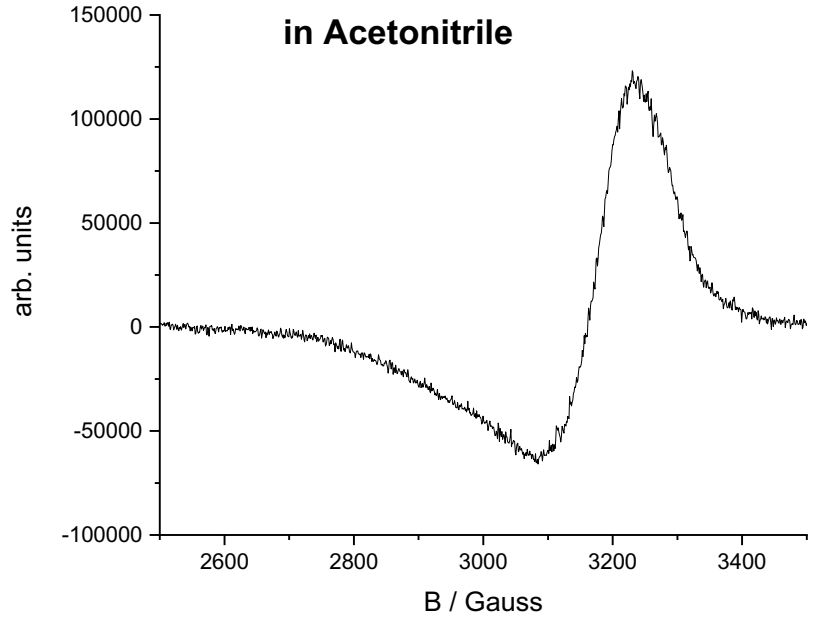


Figure S14: Cu^{II}-complex **4** (12.5 mmol/L) in acetonitrile (2.0 mL), water (45 µL, 2.2 Vol%) 78 K. The sum of 16 measurements is plotted.

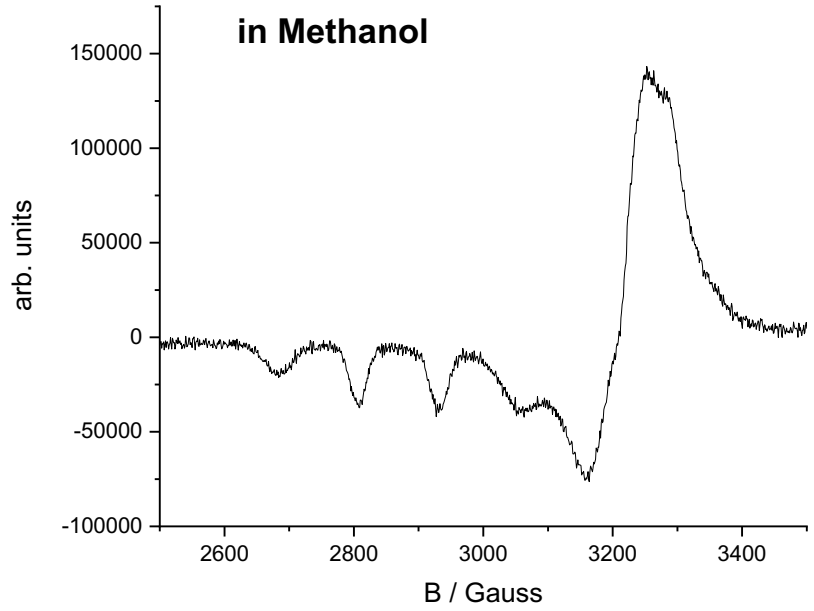


Figure S15: Cu^{II}-complex **4** (12.5 mmol/L) in MeOH (2.0 mL), water (45 µL, 2.2 Vol%) 78 K. The sum of 16 measurements is plotted.

11 Computational Chemistry

11.1 General Information

All calculations were conducted using the gaussian16[12] software package. Density functional theory calculations were carried out with the Becke-style 3-Parameter Density Functional Theory using the Lee-Yang-Parr correlation functional (B3LYP).[13] The final structures were calculated with the addition of *Grimme's* empirical dispersion correction D3.[14] For the atoms H, C, N, O the Pople-type triple zeta valence basis set 6-311G(d,p)[15] was used, while for Cu atoms the Ahlrichs-Weigend triple zeta valence polarisation basis set Def2-TZVP[16] was used. Stationary points were confirmed as local minima by frequency calculations (no imaginary frequencies). Wavefunctions of open shell molecules were checked for stability by using the keyword stable. Gibbs free energies were obtained by the sum of electronic and thermal free energies. UV/Vis simulations were done with the TD-DFT approach using the same level of theory stated above. Visualization of geometries was achieved with GaussView[17] (Version 6.0.16).

11.2 Simulated UV/Vis Spectra

All data for the calculated UV/Vis spectra were printed from GaussView and visualized with Origin 2019b (Version 9.6.5.169).

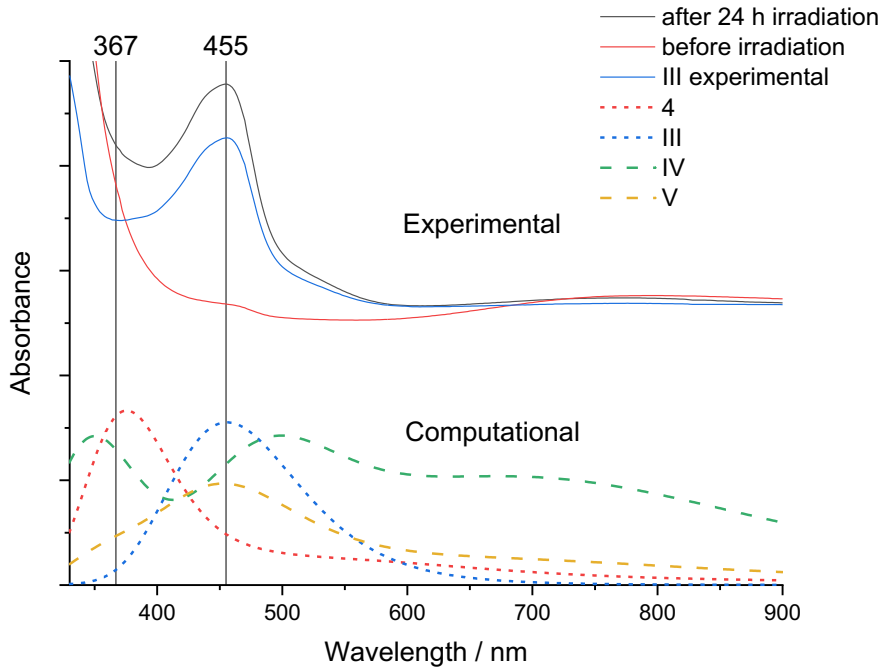
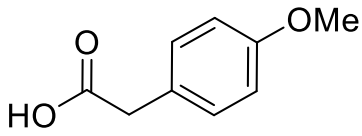
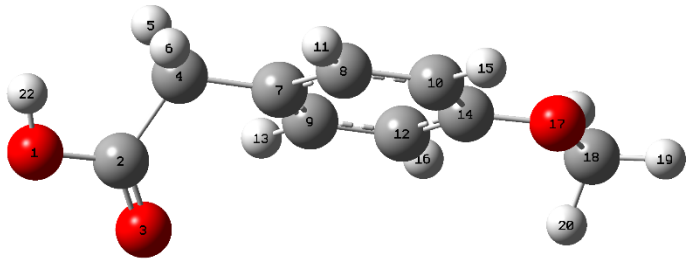


Figure S16: Comparison between experimental and calculated UV/Vis spectra.

11.3 Optimized xyz-Matrices and Thermodynamic Data

1a





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 O                 -2.60360500   -1.35672900    0.77159200
 C                 -2.13564300    0.59852600   -0.59529900
 H                 -2.37664600    0.42224700   -1.65251600
 H                 -2.46679000    1.61923100   -0.37627200
 C                 -0.65192500    0.47564700   -0.35923400
 C                  0.08925900    1.56349200    0.11363400
 C                  0.02140200   -0.71844300   -0.61346400
 C                  1.45714900    1.46624500    0.32143000
 H                 -0.41009600    2.50385900    0.32504800
 C                  1.39458100   -0.83471200   -0.40923100
 H                 -0.53471400   -1.58238900   -0.95589300
 C                  2.12166000    0.26348100    0.06081100
 H                  2.03482800    2.30550300    0.68860200
 H                  1.87911600   -1.77975300   -0.61270700
 O                  3.46437000    0.26490400    0.29600300
 C                  4.19261000   -0.93465000    0.07073100
 H                  5.22603300   -0.70781700    0.32811800
 H                  3.83197800   -1.75040500    0.70804400
 H                  4.14219200   -1.24578600   -0.97938000
 H                 -4.49483900    0.72317300   -0.29393100
```

```
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 Thermal correction to Enthalpy=                  0.187386
 Thermal correction to Gibbs Free Energy=         0.136514
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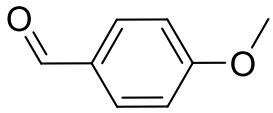
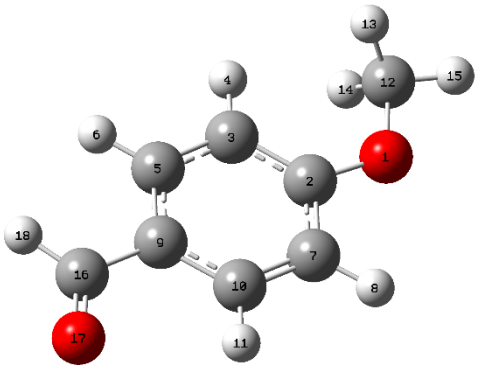
2a





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C	-0.53824900	-1.28541600	-0.00026600
H	-0.89735800	-2.31019500	-0.00014500
C	0.37295200	1.34423200	-0.00022800
H	0.76316300	2.35450000	-0.00015400
C	-1.45693900	-0.23522800	-0.00013500
C	-0.98153700	1.08781300	-0.00014600
H	-1.70490100	1.89464100	-0.00007700
C	3.59467800	-0.37766700	0.00073900
H	3.52483400	-1.00568800	-0.89417100
H	3.52318800	-1.00546000	0.89567700
H	4.54963400	0.14438500	0.00153800
C	-2.90467400	-0.50896200	-0.00004600
O	-3.77095300	0.33800700	0.00070100
H	-3.16820800	-1.59057700	-0.00086900

Zero-point correction=	0.142038	(Hartree/Particle)
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Thermal correction to Gibbs Free Energy=	0.108138	
Sum of electronic and zero-point Energies=	-460.089443	
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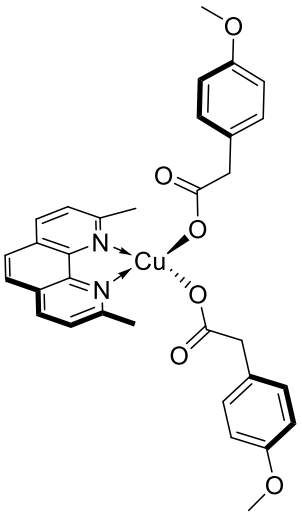
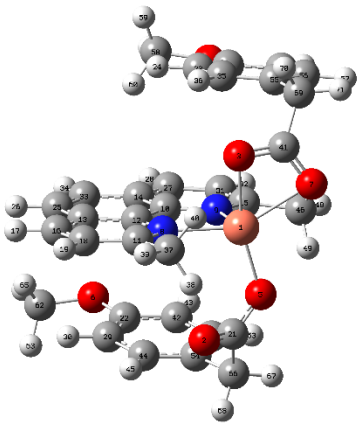
4





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O	-1.08763600	-2.34337900	-1.68928900
O	-2.91065000	3.74810800	-0.51695900
O	2.05874200	-2.87156300	-1.21443300
N	-0.87515400	-1.50340100	1.31296500
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C	-0.16331800	0.63892100	0.44548400
C	-1.46485900	-2.26725700	2.23023500
C	-0.85814900	-0.15350000	1.43803800
C	-1.49817600	0.50017500	2.51612700
C	-0.14978200	2.04732900	0.56913400
C	1.00705900	0.68451800	-1.55297500
C	-2.15692900	-0.31203800	3.46101500
H	-2.66832200	0.15154500	4.29816100
C	-2.13526300	-1.67927500	3.32380300
H	-2.62306800	-2.32003300	4.04712400
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C	-2.36252600	-2.41524100	-1.46898400
C	-3.05794600	2.45373300	-0.94840500
C	3.50496200	1.24872900	1.20683800
H	3.04526500	1.76615800	2.03746400
C	-1.45179000	1.92910300	2.61204700
H	-1.94887100	2.40475600	3.45059400
C	0.50844600	2.76853000	-0.44726800
H	0.53808900	3.85110700	-0.39939500
C	-3.78021800	1.47003200	-0.27022700
H	-4.28798200	1.69100300	0.65873000
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H	1.57830900	2.63297600	-2.29509000
C	-0.80333400	2.67264200	1.67674800
H	-0.78448700	3.75429300	1.74347700
C	3.54832500	-0.14267900	1.21330200
H	3.09792300	-0.68464600	2.03598900
C	-1.37695900	-3.74995500	2.04989400
H	-1.89379400	-4.00674200	1.12028100
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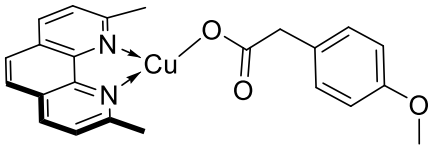
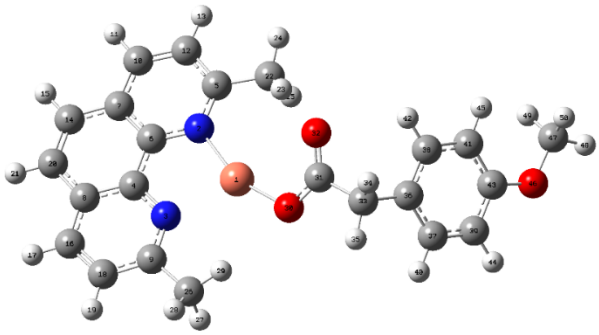
5





0 1

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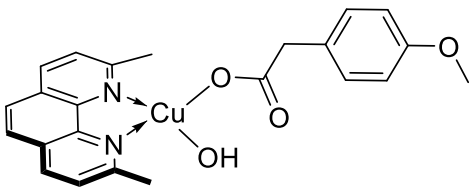
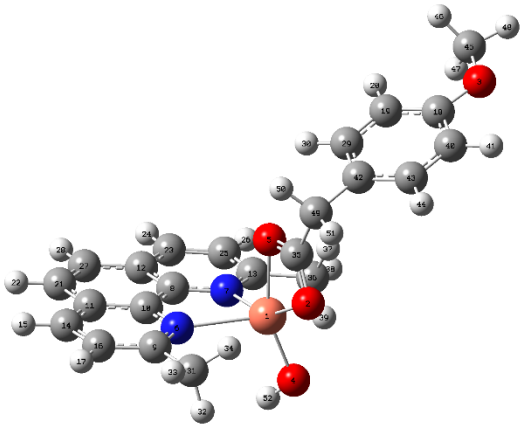
C	-3.65355400	-0.32942200	-0.29685800
C	-1.48422900	2.54976700	0.19198600
C	-3.23419100	1.04542300	-0.14706600
C	-4.20279300	2.07149000	-0.19784800
C	-5.02069800	-0.62507800	-0.49138300
C	-3.02857400	-2.56427600	-0.35261400
C	-3.74000900	3.39458100	-0.03476500
H	-4.44742500	4.21653900	-0.06188200
C	-2.39923900	3.62752800	0.15877700
H	-2.02569500	4.63572300	0.28677800
C	-5.58108700	1.73604000	-0.40113500
H	-6.30759200	2.54028700	-0.43791500
C	-5.36100300	-1.99052000	-0.61943900
H	-6.39843400	-2.27071000	-0.76843400

C	-4.37805500	-2.94892200	-0.54879500
H	-4.62120700	-4.00081800	-0.64062100
C	-5.97526900	0.44133600	-0.54252900
H	-7.02075900	0.19634200	-0.69402500
C	-0.01203800	2.76945600	0.36685800
H	0.42087500	2.03017200	1.04966900
H	0.20074300	3.77972200	0.72018800
H	0.49194800	2.62893900	-0.59559500
C	-1.92237700	-3.57977600	-0.29048400
H	-1.69059800	-3.94038800	-1.29856400
H	-2.21900400	-4.44585500	0.30660200
H	-1.01660600	-3.13638300	0.12669600
O	0.80331100	-1.39391100	0.58709700
C	1.68446700	-0.82614500	1.34222300
O	1.58004400	0.28367600	1.87235300
C	2.97368100	-1.63473800	1.54658600
H	3.21378800	-1.60176300	2.61348000
H	2.80423400	-2.67226100	1.25762300
C	4.11693200	-1.04649100	0.74534700
C	4.73875200	-1.77246600	-0.27645400
C	4.57102900	0.24981500	0.99455600
C	5.78151000	-1.23071000	-1.01668100
H	4.39929900	-2.77913400	-0.49770100
C	5.61650700	0.80960800	0.26099600
H	4.07503300	0.83436600	1.76021300
C	6.23005200	0.06567300	-0.75094900
H	6.26531900	-1.79151700	-1.80751500
H	5.93820500	1.81763800	0.48683900
O	7.26461300	0.51068200	-1.53094100
C	7.76025500	1.81936700	-1.30340500
H	8.56775300	1.96312200	-2.02057800
H	6.98887700	2.58095900	-1.47258500
H	8.15730100	1.93215600	-0.28696900

Zero-point correction=	0.391205 (Hartree/Particle)
Thermal correction to Energy=	0.418152
Thermal correction to Enthalpy=	0.419096
Thermal correction to Gibbs Free Energy=	0.328289
Sum of electronic and zero-point Energies=	-2864.928845
Sum of electronic and thermal Energies=	-2864.901898
Sum of electronic and thermal Enthalpies=	-2864.900954
Sum of electronic and thermal Free Energies=	-2864.991762

8





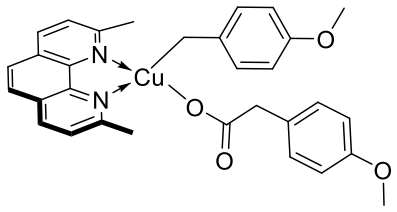
0 2

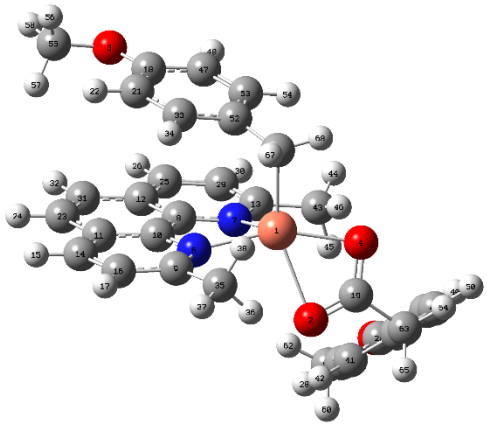
Cu	0.67077500		
0.58570200	-1.24073300		
O	-0.69021300	2.27435100	-0.96929100
O	-6.92021900	-0.94698400	0.35829600
O	1.11725400	0.58184000	-3.04283300
O	-0.53120500	0.57926300	0.41625400
N	2.59025100	1.10597900	-0.02822500
N	1.49336400	-1.28686300	-0.73479200
C	2.55945000	-1.28807300	0.09445500
C	3.09507900	2.29233000	0.28137100
C	3.13853100	-0.01763600	0.47645800
C	4.25228500	-0.00132400	1.34762600
C	3.12554800	-2.48681400	0.58582900
C	0.93475800	-2.42645700	-1.13004300
C	4.77465300	1.26674500	1.68204700
H	5.62519500	1.33425500	2.35222900
C	4.20396200	2.40179100	1.15507900
H	4.59393400	3.38267400	1.39841500
C	-5.75572700	-0.25125100	0.52603800
C	-4.59971800	-0.76243200	1.12363000
H	-4.56578100	-1.77708400	1.49718200
C	4.79162300	-1.23519700	1.83727700
H	5.64433500	-1.19870500	2.50641800
C	2.53022900	-3.69378600	0.16239800
H	2.93290700	-4.63836200	0.51260000
C	1.44967000	-3.66543400	-0.68894400
H	0.98204500	-4.58238900	-1.02510800
C	4.25275700	-2.42856400	1.46903300
H	4.66863900	-3.35940100	1.83854100
C	-3.46876200	0.04444500	1.24338300
H	-2.56578500	-0.36082900	1.68409300
C	2.46206000	3.49472400	-0.35820300
H	2.84535700	3.60770100	-1.37772200
H	2.68270800	4.40913000	0.19523900
H	1.38254800	3.35872600	-0.44521600
C	-1.07981900	1.67580300	0.06571600
C	-0.25316600	-2.31334100	-2.03821000
H	-1.09097400	-1.88236900	-1.47971300
H	-0.55478400	-3.28080700	-2.44040700
H	-0.02053500	-1.61330100	-2.84757600
C	-5.75894300	1.06380300	0.05189300
H	-6.66127100	1.44167400	-0.41328900
C	-3.46115900	1.36015300	0.77923800
C	-4.62416400	1.85296200	0.17783900

H	-4.64095300	2.86919200	-0.20155300
C	-6.97365100	-2.29017000	0.81246500
H	-6.81050600	-2.35850900	1.89494100
H	-6.23901700	-2.92110700	0.29738700
H	-7.97653200	-2.64505000	0.57866500
C	-2.22031500	2.22376600	0.90452000
H	-1.88432500	2.24809100	1.94595500
H	-2.42841500	3.24352000	0.58072100
H	1.98740400	0.19978500	-3.19419600

Zero-point correction= 0.404617 (Hartree/Particle)
Thermal correction to Energy= 0.433531
Thermal correction to Enthalpy= 0.434475
Thermal correction to Gibbs Free Energy= 0.340307
Sum of electronic and zero-point Energies= -2940.745962
Sum of electronic and thermal Energies= -2940.717048
Sum of electronic and thermal Enthalpies= -2940.716104
Sum of electronic and thermal Free Energies= -2940.810272

6





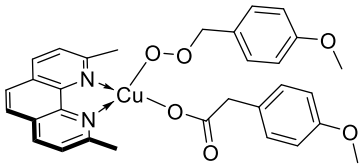
0 2

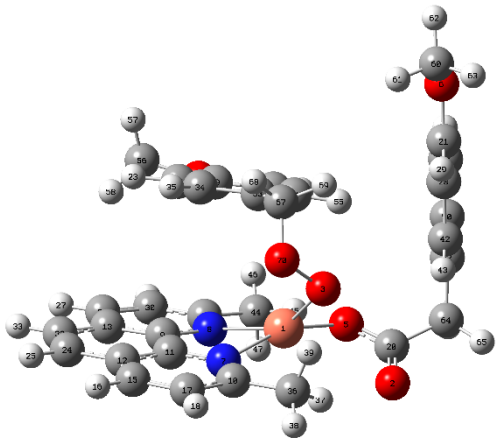
Cu	-0.01179000		
1.73332700	-0.62723400		
O	1.78940400	2.56381300	0.52121400
O	-4.32746400	-2.94146500	-1.20259200
O	1.74426800	2.08080800	-1.63754600
O	5.86273700	-2.72966600	0.62321800
N	-1.36294300	1.69821600	0.94682300
N	-0.01806500	-0.49736100	0.05540300
C	-1.10394700	-0.69001700	0.83595200
C	-1.93772900	2.80064200	1.42171200
C	-1.79894000	0.47643700	1.33221700
C	-2.90950800	0.31353200	2.19306100
C	-1.59199800	-1.97307000	1.16909100
C	0.63573600	-1.54319100	-0.43314900
C	-3.52269100	1.48619100	2.67574500
H	-4.37728600	1.40776000	3.33952500
C	-3.03284300	2.71954200	2.30569400
H	-3.48295700	3.63143400	2.67791300
C	-3.72611600	-1.74331700	-1.49146100
C	2.37489400	2.40053900	-0.57708600
C	5.37701000	-1.47104500	0.40103100
C	-4.17619700	-0.49694000	-1.05357500

H	-5.08064300	-0.40378000	-0.46779700
C	-3.36983300	-1.00494600	2.51181100
H	-4.23392000	-1.10865200	3.15913700
C	-0.89476200	-3.07691900	0.63487400
H	-1.24556800	-4.08169800	0.84389100
C	4.66014100	-0.71598800	1.33469200
H	4.44495300	-1.10384200	2.32121500
C	0.20989900	-2.86451300	-0.15304400
H	0.75839800	-3.69708800	-0.57708000
C	-2.74462300	-2.10255300	2.00800900
H	-3.10600400	-3.09876100	2.23802800
C	-3.43283100	0.64591100	-1.34082300
H	-3.77767300	1.60238100	-0.96107400
C	-1.36704800	4.10948200	0.95835200
H	-0.27749600	4.08222000	1.04506300
H	-1.76690800	4.95105000	1.52518700
H	-1.59712900	4.25679600	-0.10163600
C	5.62800100	-0.93586600	-0.86625300
H	6.18087700	-1.53627900	-1.57854300
C	4.20656800	0.55725400	0.99153500
H	3.62213400	1.12826800	1.70366100
C	1.84238200	-1.28228500	-1.28520500
H	1.93409500	-2.02983000	-2.07662400
H	2.74911700	-1.33269300	-0.67480100
H	1.79981800	-0.28325800	-1.71878800
C	-2.55897800	-1.81622300	-2.26305100
H	-2.23358500	-2.78977600	-2.60945700
C	5.16726900	0.33308700	-1.19139500
H	5.35832300	0.72835300	-2.18332400
C	4.45151300	1.10351700	-0.26908600
C	-2.22640400	0.59633900	-2.06081400
C	-1.83304500	-0.67418900	-2.54214000
H	-0.91403000	-0.75322900	-3.11325800
C	-5.54783800	-2.91630500	-0.47984900
H	-6.32422200	-2.35860300	-1.01755100
H	-5.41605600	-2.47892600	0.51727900
H	-5.85871200	-3.95562400	-0.37846200
C	5.63090500	-3.32538300	1.89046400
H	6.08772700	-2.74459000	2.70070300
H	6.09704600	-4.30887400	1.84809500
H	4.55905300	-3.44234500	2.09257600
C	3.89525600	2.46693000	-0.63593000
H	4.20991500	2.74831100	-1.64131700
H	4.23671200	3.22389200	0.07425300
C	-1.36114500	1.76156900	-2.20100700
H	-1.87377800	2.72189000	-2.12337800
H	-0.67338800	1.73577700	-3.04581400

Zero-point correction=	0.541133 (Hartree/Particle)
Thermal correction to Energy=	0.577080
Thermal correction to Enthalpy=	0.578025
Thermal correction to Gibbs Free Energy=	0.470346
Sum of electronic and zero-point Energies=	-3250.366158
Sum of electronic and thermal Energies=	-3250.330210
Sum of electronic and thermal Enthalpies=	-3250.329266
Sum of electronic and thermal Free Energies=	-3250.436945

7





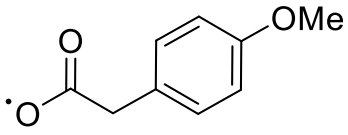
0 2

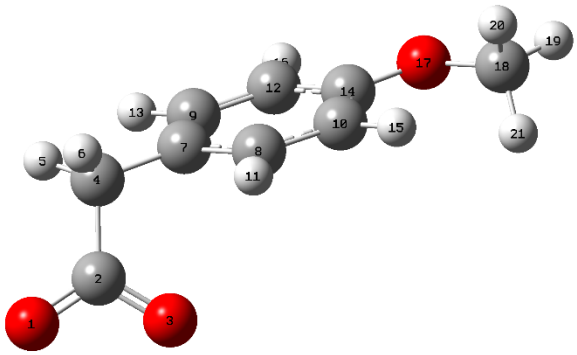
Cu	-0.39388100	-1.06411900	-0.79715700
O	1.27407700	-2.83521200	-2.35211500
O	0.78611800	-1.89140900	0.50236000
O	-0.33383500	4.26940800	-0.16397200
O	1.02973000	-0.62817400	-2.01900800
O	5.60085200	1.07416900	1.82425300
N	-2.08195600	-1.93140000	-0.02724700
N	-1.87421600	0.51388500	-1.16800400
C	-2.96573100	0.26236000	-0.39781700
C	-2.16484000	-3.17915100	0.42787300
C	-3.07555100	-1.04115000	0.20821300
C	-4.21088300	-1.36026000	0.98184300
C	-3.99975800	1.20123100	-0.19898400
C	-1.77013600	1.67869000	-1.79912500
C	-4.28102500	-2.67567100	1.49186700
H	-5.13311900	-2.96958000	2.09565300
C	-3.28342200	-3.57306600	1.20293100
H	-3.33095900	-4.59158500	1.56752600
C	-0.09744000	3.11509100	0.53900100
C	1.70684700	-1.68800600	-2.35494200
C	5.02808300	0.41183000	0.77285800
C	-0.92128600	2.63288700	1.55908000
H	-1.80448600	3.17479700	1.86871300
C	-5.22268500	-0.37059900	1.19285200
H	-6.08006600	-0.62752900	1.80498300
C	-3.86539600	2.44339300	-0.85851600
H	-4.63376300	3.19981000	-0.73629300
C	4.52682100	-0.89146500	0.82898600
H	4.56165600	-1.46634900	1.74448500
C	-2.77239000	2.67210300	-1.65252000
H	-2.64656800	3.61304000	-2.17281000
C	-5.11993500	0.86220300	0.62504600
H	-5.89436200	1.60598100	0.77705700
C	-0.60107400	1.42539900	2.17963700
H	-1.24695700	1.05090400	2.96777400
C	-1.05910700	-4.14228600	0.12532000
H	-0.53203000	-3.87544200	-0.79181600
H	-1.44927700	-5.16061500	0.06146600
H	-0.31771000	-4.08939200	0.92632100
C	4.94338600	1.12764500	-0.42509100
H	5.32824200	2.14007600	-0.44824600

C	3.94864000	-1.45975000	-0.30563300
H	3.51401200	-2.45002200	-0.23509400
C	-0.59512200	1.93784400	-2.69113000
H	0.18651600	1.19517900	-2.54389800
H	-0.20731100	2.94097700	-2.50052800
H	-0.92194800	1.89850200	-3.73661400
C	1.02870300	2.38567400	0.14942700
H	1.65017100	2.76614400	-0.65060600
C	4.36520700	0.54426100	-1.54506100
H	4.29249400	1.11816900	-2.46306900
C	3.86092500	-0.76015700	-1.50949500
C	0.52419500	0.69166300	1.80688400
C	1.33077100	1.18540500	0.77251800
H	2.18519700	0.61275200	0.44023700
C	-1.29971900	5.17779000	0.34543900
H	-1.07052100	5.46530500	1.37775100
H	-2.31174500	4.75877200	0.30419300
H	-1.25128500	6.05791200	-0.29478600
C	5.63916000	0.42285000	3.08374300
H	4.63148300	0.18046500	3.44333700
H	6.10509400	1.12766600	3.77138100
H	6.23841500	-0.49514800	3.04894700
C	3.16902200	-1.38413100	-2.70263300
H	3.64958300	-2.31775900	-3.00110600
H	3.19320400	-0.69421700	-3.55044200
C	0.83679500	-0.63568100	2.44620700
H	0.45490400	-0.67839400	3.47101900
H	1.91651000	-0.81598800	2.45244600
O	0.19581500	-1.73803800	1.79518800

Zero-point correction= 0.551196 (Hartree/Particle)
Thermal correction to Energy= 0.588741
Thermal correction to Enthalpy= 0.589685
Thermal correction to Gibbs Free Energy= 0.478509
Sum of electronic and zero-point Energies= -3400.769760
Sum of electronic and thermal Energies= -3400.732215
Sum of electronic and thermal Enthalpies= -3400.731271
Sum of electronic and thermal Free Energies= -3400.842447

9





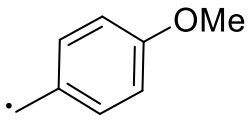
0 2

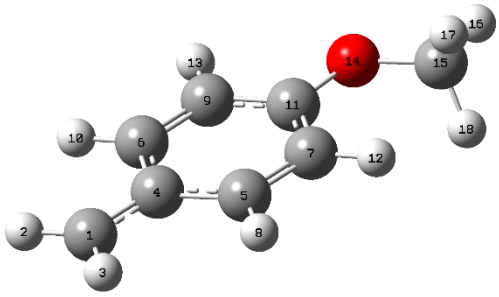
O	-4.21888100	0.24169300	0.37288800
C	-2.98794200	0.30273600	0.20909900
O	-2.38757600	1.17022000	0.90639300
C	-2.22542200	-0.56734500	-0.77074300

H	-2.60365000	-1.58908100	-0.69334200
H	-2.47562900	-0.21456500	-1.77688200
C	-0.74630400	-0.47961400	-0.49913300
C	-0.04258700	0.69786600	-0.77842600
C	-0.04812000	-1.54592800	0.08455300
C	1.31707400	0.81541900	-0.50533000
H	-0.56670600	1.53831000	-1.21803700
C	1.30346300	-1.44703900	0.35976500
H	-0.57346500	-2.46491900	0.32113700
C	1.99898900	-0.26190100	0.06826000
H	1.82597200	1.74059100	-0.73706400
H	1.85381200	-2.26792000	0.80242600
O	3.31977400	-0.26900000	0.37771500
C	4.08611300	0.90634000	0.13344900
H	5.09649500	0.67442400	0.46497300
H	4.10265600	1.15794400	-0.93284500
H	3.70238800	1.75870400	0.70471000

Zero-point correction= 0.161477 (Hartree/Particle)
Thermal correction to Energy= 0.172561
Thermal correction to Enthalpy= 0.173506
Thermal correction to Gibbs Free Energy= 0.122488
Sum of electronic and zero-point Energies= -573.991090
Sum of electronic and thermal Energies= -573.980006
Sum of electronic and thermal Enthalpies= -573.979062
Sum of electronic and thermal Free Energies= -574.030079

10





0 2

C	-3.30009000	-0.31693700	0.00042900
H	-3.98295000	0.52325400	0.00063400
H	-3.72452900	-1.31303500	0.00049700
C	-1.91180000	-0.12128400	-0.00000100
C	-0.99947200	-1.21281800	-0.00024900
C	-1.33771900	1.18715700	-0.00008900
C	0.37320000	-1.02395800	-0.00035000
H	-1.39420900	-2.22321600	-0.00041900
C	0.02427900	1.37726000	-0.00014100
H	-1.99814900	2.04767300	-0.00011300
C	0.90043700	0.27572900	-0.00018200
H	1.02536900	-1.88711900	-0.00069600
H	0.45659800	2.37072100	-0.00021200
O	2.22760700	0.57968700	-0.00003700
C	3.16936000	-0.48511200	0.00041400
H	4.15097600	-0.01403100	0.00100500
H	3.06796400	-1.11107400	0.89459900

```
 H                  3.06889800   -1.11089600   -0.89398500

Zero-point correction=                   0.146717 (Hartree/Particle)
 Thermal correction to Energy=                    0.154910
 Thermal correction to Enthalpy=                  0.155855
 Thermal correction to Gibbs Free Energy=         0.113506
 Sum of electronic and zero-point Energies=        -385.402916
 Sum of electronic and thermal Energies=           -385.394722
 Sum of electronic and thermal Enthalpies=         -385.393778
 Sum of electronic and thermal Free Energies=      -385.436127
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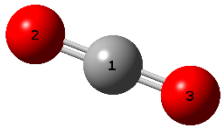
CO_2

O=C=O

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0 1
 C                  0.00000000    0.00000000    0.00000000
 O                  0.00000000    0.00000000    1.16052400
 O                  0.00000000    0.00000000   -1.16052400

Zero-point correction=                   0.011717 (Hartree/Particle)
 Thermal correction to Energy=                    0.014340
 Thermal correction to Enthalpy=                  0.015284
 Thermal correction to Gibbs Free Energy=        -0.008977
 Sum of electronic and zero-point Energies=        -188.629601
 Sum of electronic and thermal Energies=           -188.626979
 Sum of electronic and thermal Enthalpies=         -188.626035
 Sum of electronic and thermal Free Energies=      -188.650295
```
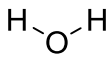
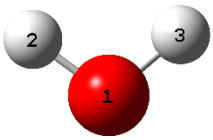

H_2O

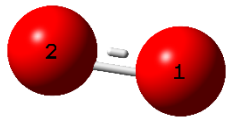





```
0 1
 O                  0.00000000    0.00000000    0.11865100
 H                  0.00000000    0.75700000   -0.47460500
 H                  0.00000000   -0.75700000   -0.47460500

Zero-point correction=                   0.021323 (Hartree/Particle)
 Thermal correction to Energy=                    0.024158
 Thermal correction to Enthalpy=                  0.025102
 Thermal correction to Gibbs Free Energy=         0.003676
 Sum of electronic and zero-point Energies=         -76.426134
 Sum of electronic and thermal Energies=            -76.423299
 Sum of electronic and thermal Enthalpies=          -76.422354
 Sum of electronic and thermal Free Energies=       -76.443780
```

O_2

O=O




```
0 3
 O                  0.00000000    0.00000000    0.60281900
 O                  0.00000000    0.00000000   -0.60281900
```

```
Zero-point correction=                          0.003738 (Hartree/Particle)
 Thermal correction to Energy=                    0.006101
 Thermal correction to Enthalpy=                  0.007045
 Thermal correction to Gibbs Free Energy=        -0.016227
 Sum of electronic and zero-point Energies=      -150.361051
 Sum of electronic and thermal Energies=         -150.358688
 Sum of electronic and thermal Enthalpies=       -150.357743
 Sum of electronic and thermal Free Energies=    -150.381016
```

12 Additional Spectroscopic Investigations

12.1 Steady-State Absorption Spectroscopy

Static absorption spectra were measured with a Cary 60 spectrophotometer (Agilent technologies) using 1 cm^2 quartz optical cells. Photolysis was carried out using a 427 nm Kessil LED lamp placed at a 10 cm distance. All solvents used were fresh and spectrophotometric grade.

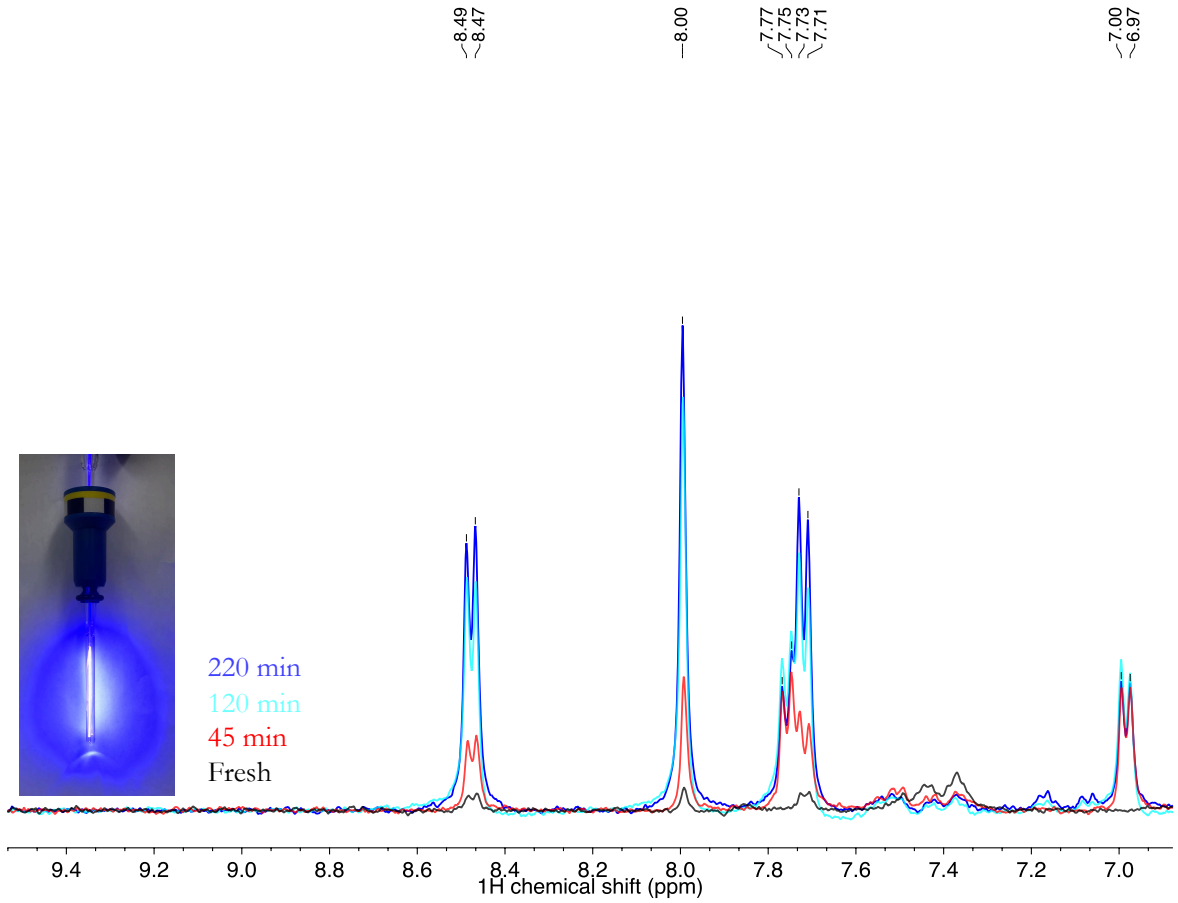


Figure S17: ^{1}H NMR spectra (400 MHz) of fresh and 420 nm photolyzed Cu(dmp)(1a)$_2$ (**4**) in acetonitrile showing the emergence of the Cu(I)-coordinated dmp proton peaks (8.47 ppm (doublet), 8 ppm (singlet), and 7.71 ppm (doublet)) as a function of irradiation time to generate the $[Cu(dmp)_2]^+$ species. Note that the doublets located at 6.95 and 7.75 ppm are assigned to **2a**. The photolysis was carried out in-situ using a 420 nm LED fiber optic-coupled to a capillary jacket within the 5 mm NMR tube. Irradiation times are indicated in the legend.

12.2 Steady-State FT-IR spectroscopy

Solution-phase IR spectra were recorded with Vertex 80V FTIR spectrophotometer operating with OPUS v.7.2 software using a demountable liquid IR cell having 2 CaF_2 windows and a 200 µm spacer to achieve an appropriate pathlength for these measurements. Photolysis was carried out using a 427 nm Kessil LED lamp placed at a 10 cm distance. All solvents used were fresh and spectrophotometric grade.

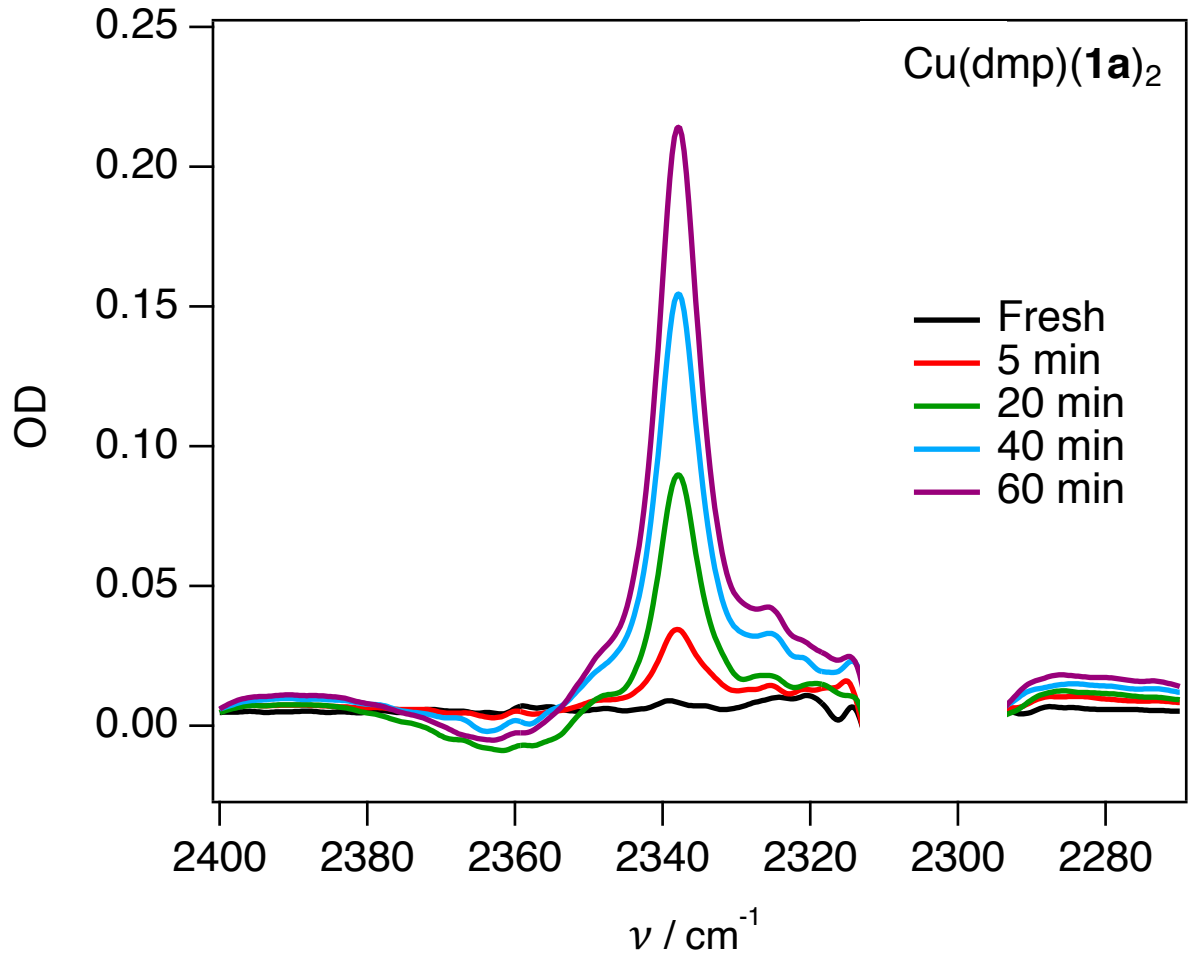


Figure S18: Solution-phase IR spectra of fresh and 427 nm photolyzed Cu(dmp)(1a)$_2$ (**4**) in dichloromethane showing the emergence of an absorbance band at 2335 cm^{-1} growing with irradiation time. This band is assigned to the proposed CO_2 release upon decarboxylation of the 4-methoxyphenylacetoxy radical species. Irradiation times are indicated in the legend.

12.3 NMR Photolysis

^{1}H NMR spectra were acquired on Bruker NEO 400 MHz NMR spectrometer. Photolysis was carried out *in-situ* inside the NMR tube using a fiber-coupled 420 nm LED system (Prizmatix FC5-LED light source).

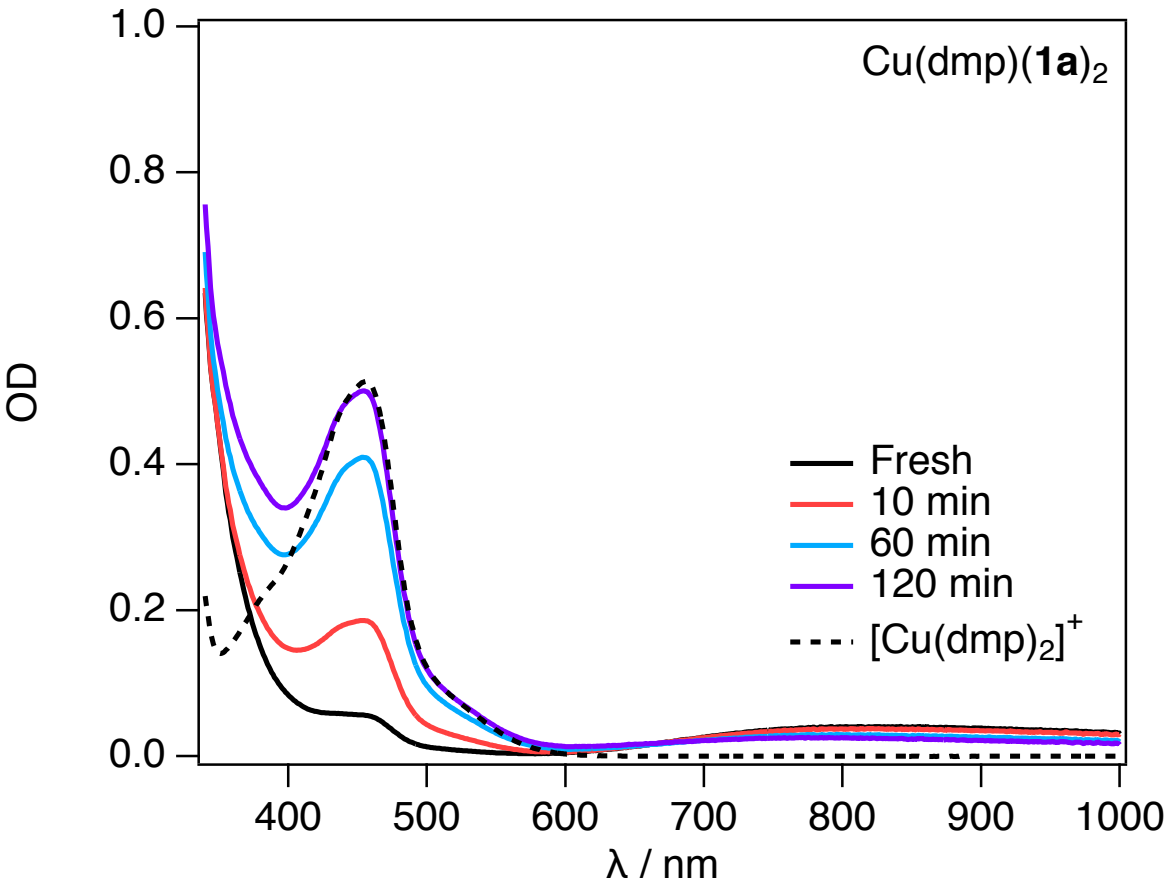


Figure S 19: UV-vis absorption spectra of fresh and 427 nm photolyzed Cu(dmp)(1a)$_2$ (**4**) in acetonitrile. Irradiation times are indicated in the legend. The spectrum of independently prepared $[Cu(dmp)_2]^+$ (dashed line) is overlayed for comparison.

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